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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re the Application of:

JOHNSON et al.

Serial No.: 10/622,677

Filed: July 18, 2003

Atty. File No.: 3791-13-CON

For: "LOW SULFUR COAL ADDITIVE  
FOR IMPROVED FURNACE  
OPERATION"

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313

) Group Art Unit: 3749  
)

) Examiner: RINEHART, KENNETH  
)

) DECLARATION OF  
) MICHAEL DURHAM  
) UNDER 37 C.F.R. §1.132  
)

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DATE OF DEPOSIT: July 29, 2004

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Dear Sir:

I, Michael Durham, state as follows:

1. I received a Bachelor of Science in Aerospace Engineering from Pennsylvania State University in 1971; a Master of Engineering in Environmental Engineering from the University of Florida in 1975; a Ph. D. in Environmental Engineering from the University of Florida in 1978; and a Master of Business Administration from the University of Denver in 1997.

2. I have been previously employed by the National Academy of Sciences (1972-1973), the American Psychological Association (1973-1974), Environmental Engineering Consultants (1975-1978), Denver Research Institute (1978-1985, and ADA Technologies, Inc. (1985-1996) (of which I was I founder and Executive Vice President). I am a cofounder and President of ADA Environmental Solutions, LLC, and a shareholder, President, and member of the Board of Directors of ADA Environmental Solutions, Inc. ADA Environmental Solutions, Inc., was founded in 1996 to commercialize environmental technologies to help existing coal fired-boilers meet more stringent environmental regulations. ADA Environmental Solutions,

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LLC, the owner of the above patent application, is a wholly owned subsidiary of ADA Environmental Solutions, LLC.

3. For the past 28 years, including during my employment by Environmental Engineering Consultants, ADA Technologies, Inc., and ADA Environmental Solutions, Inc., I have been involved in the measurement and control of air pollution from utility and industrial sources. The majority of this work was directed at reducing emissions of particulates, sulfur oxides, nitrogen oxides, and mercury from coal-fired boilers.

4. I have received numerous honors in the area of air and waste management, with specific emphasis on coal-fired utilities. For example, from 1989 to 1990 I was Chairman of the Rocky Mountain States Section of the Air and Waste Management Association (A&WMA), from 1994 to 1996 I was Chairman of the A&WMA National Technical Committee on Control of Particulate Matter and Acid Gases, and from 1999 to 2002, I was Chairman of the A&WMA Emission Control Division. I was the 2001 winner of the A&WMA Sensenbaugh Award for Air Pollution Control Technology and the 2003 winner of an R&D 100 Award for Mercury Control Technology for coal-fueled boilers. In 2001, I was appointed by the DOE Secretary Abraham to the National Coal Council. I have published over 180 papers related to air pollution measurement and control.

5. I submit that I am qualified to testify as to the understanding of one of ordinary skill in the relevant arts of air and waste management and utility design and operation at the time the above-identified application and the provisional application (from which the above-identified application claims priority) were filed.

6. In connection with the Office Action mailed January 29, 2004, I reviewed the following documents: (a) the Office Action; (b) U.S. Patent 6,484,651 to Shepard, Jr., et al. ("the Shepard Patent"); (c) the above application ("the Subject Application"); and (d) U.S. Provisional Application Serial No. 60/213,915, filed June 26, 2000, entitled "Low-Cost Technology to

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Improve Operation of Cyclone Furnaces Firing Low-Sulfur Western Coals” (“Provisional Application”) from which the Subject Application claims priority.

7. At pages 3-5 of the Office Action, the Examiner states that the sub-bituminous coal limitation of dependent claims 2 and 20 of the Subject Application, namely that “the solid fuel comprises a sub-bituminous coal”, fails to comply with the written description requirement of 35 U.S.C. § 112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

8. I disagree. The Subject and Provisional Applications each reference coals from the Powder River Basin of Montana and Wyoming (Provisional Application at pages 3-5 and 8; Subject Application at page 1, lines 8-11) and the Subject Application refers specifically to “sub-bituminous coal” as the solid fuel feed (Subject Application at page 6, line 9). Because coal in the Powder River Basin is primarily sub-bituminous coal, the reference to the Powder River Basin would convey to one skilled in the relevant art that the inventors, at the time the Provisional and Subject Applications were filed, had possession of the invention claimed in claims 2 and 20.

9. At page 4 of the Office Action, the Examiner states that the cyclone boiler limitation of claim 5, namely that the boiler is a cyclone boiler, fails to comply with the written description requirement of 35 U.S.C. § 112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

10. I disagree. The Subject and Provisional Applications each specifically refer not only to the general class of boiler that includes the cyclone boiler, namely wet-bottom boilers, (Provisional Application at page 2; Subject Application at page 6, lines 15-18) but also



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specifically to cyclone boilers (Provisional Application at pages 1-5 and 7-8 and Subject Application at Figure 1, page 1, line 24 to page 2, line 19, page 5, lines 16-17, and page 6, lines 15-18). These references would convey to one skilled in the relevant art that the inventors, at the time the Provisional and Subject Applications were filed, had possession of the invention claimed in claim 5.

11. At page 4 of the Office Action, the Examiner states that the pulverizing limitation of claim 7, namely that the solid fuel is pulverized prior to being introduced into the boiler, fails to comply with the written description requirement of 35 U.S.C. § 112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

12. I disagree. The Subject Application discloses a “slag type” furnace in which a slag layer forms on a surface of the burner and captures coal particles for combustion. (Subject Application at page 1, lines 21-23) Both the Subject and Provisional Applications disclose a cyclone furnace or boiler *and* wet-bottom boilers as noted in Paragraph 10 above. “Pulverized” coal boilers include both wet-bottom and dry-bottom boilers using a pulverized coal feed. A cyclone boiler is a type of wet-bottom boiler for which the coal feed is crushed but not pulverized. A cyclone boiler is the only type of wet-bottom boiler which uses crushed but not pulverized coal feed. While it is true that pulverizers and crushers are differing types of devices and produce different size distributions of coal feed, the reference to the genus “wet-bottom boilers” would reasonably convey to one skilled in the relevant art that the inventors, at the time the Provisional and Subject Applications were filed, had possession of the subject matter of claim 7.

13. At page 4 of the Office Action, the Examiner states that the subject matter of claim 12, namely that the boiler includes a pulverizer and a fuel transfer system communicating with the pulverizer and the burner, fails to comply with the written description requirement of 35

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U.S.C. §112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

14. I disagree. As noted previously, the Specifications of the Provisional and Subject Applications reasonably convey to one skilled in the relevant art that the inventors, at the time the Provisional and Subject Applications were filed, had possession of wet-bottom boilers, whether using pulverized or crushed coal feed. It necessarily follows that the pulverizer is located upstream of the combustion chamber. The burner is disclosed at page 2 of the Provisional Application and in Figure 1 of the Subject Application. The fuel transfer system is disclosed at page 7 of the Provisional Application and in Figures 4-5 and pages 14, lines 7-13 (coal feed pipes 244a,b) and 17, lines 14-15 (coal feed lines 344a,b). Finally, the combustion chamber is described at page 2 of the Provisional Application and in Figure 1 and at page 1, line 28, and page 2, lines 7-9, (combustion chamber 108) of the Subject Application.

15. I have reviewed proposed Figure 9 and find it to be supported by both the Provisional and Subject Applications.

16. For at least the reasons set forth above, the subject matter of claim 12 is described in the Specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that the inventors, at the time each of the applications was filed, had possession of the claimed invention.

17. At page 4 of the Office Action, the Examiner states that the subject matter of claim 14, namely that the concentration of iron-bearing material to solid fuel is from about 0.5 to about 2.5 weight percent, fails to comply with the written description requirement of 35 U.S.C. §112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

18. I disagree. The Provisional Application discloses, at page 8, a concentration of iron-bearing material to solid fuel of 20 lb/ton or 1 wt.%. The Subject Application discloses at page 9, lines 6-7, iron-bearing concentrations relative to the solid fuel of 10 lb/ton (or 0.5 wt.%), 20 lb/ton (or 1.0 wt.%), and 50 lb/ton (or 2.5 wt.%). For at least the reasons set forth above, the subject matter of claim 14 is described in the Specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that the inventors, at the time each of the applications was filed, had possession of the claimed invention.

19. Finally at page 5 of the Office Action, the Examiner states that the subject matter of claim 29, namely that the concentration of carbon-containing compound in the iron bearing material is from about 0.1 to about 10 weight percent, fails to comply with the written description requirement of 35 U.S.C. § 112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

20. I disagree. This precise concentration range is disclosed in the Subject Application at page 12, lines 17-18, which discloses that the additive can include "from about 0.1 to about 10 wt.% (dry basis) greases and oils." The Provisional and Subject Applications further disclose additive carbon compound concentrations within this range at page 8 of the Provisional Application and page 15, lines 2-4, of the Subject Application (boiler slag in a concentration of about 2 to a about 20 wt.% and more preferably of about 2 to about 10 wt.%). The Subject Application discloses at page 13, lines 10-13, the addition of xanthium gum (or another organic adhesive) in a ratio of about 100:1 (or 1 wt.%) to 1000:1 (or 0.1 wt.%) parts additive to part adhesive.

21. For at least the reasons set forth above, the subject matter of claim 29 is described in the Specifications of both the Provisional and Subject Applications in such a way as to

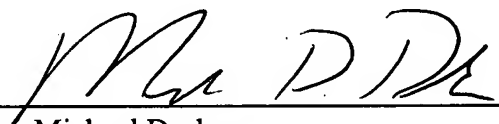
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reasonably convey to one skilled in the relevant art that the inventors, at the time each of the applications was filed, had possession of the claimed invention.

22. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Date: July 29, 2004

By:   
Michael Durham



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Reply, Application of:

JOHNSON et al.

Serial No.: 10/622,677

Filed: July 18, 2003

Atty. File No.: 3791-13-CON

For: "LOW SULFUR COAL ADDITIVE  
FOR IMPROVED FURNACE  
OPERATION"

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313

) Group Art Unit: 3749

) Examiner: RINEHART, KENNETH

) DECLARATION OF RAMON BISQUE  
) UNDER 37 C.F.R. §1.132

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Dear Sir:

I, Ramon Bisque, state as follows:

1. I received a Bachelor of Science in Chemistry from St. Norbert College in 1953; a Master of Science in Chemistry from Iowa State University in 1956; a Master of Science in Geology from Iowa State University in 1957; and a Ph. D. in Geology-Chemistry from Iowa State University in 1959.

2. I have been a certified professional geologic scientist since 1967 and am a Fellow of the American Association for the Advancement of Science.

3. From 1959 through 1990, I was a professor at the Colorado School of Mines, for which employment I have been designated as a Professor Emeritus. During 1964 through 1967, I was on leave from the Colorado School of Mines and was initially an Associate Director/Consultant and later a Director of the Earth Science Curriculum Project for the American Geological Institute. I was a co-founder of Earth Sciences, Inc., (at one time the parent of both ADA Environmental Solutions, LLC and ADA Environmental Solutions, Inc.) and have

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been employed by the company from 1972 to present. During my career, I have been involved in a wide diversity of areas including resource exploration and development, soil geochemistry, weathering, exploration geochemistry, analysis of mechanisms of silicate reactions, collection and determination of trace elements, and utility flue gas contaminant removal. Since 1997, I have been involved on behalf of ADA Environmental Solutions, Inc., in analyzing the results of full-scale testing of additives utilized in coal-fired power plants. These analyses were performed to understand the mechanisms of key reactions involved and attempt to move from the art to science” with the ultimate goal of predicting behavior of other additives.

4. In these areas, I have authored, solely or jointly with others, 27 published articles and two books.

5. I submit that I am qualified to testify as to the understanding of one of ordinary skill in the relevant arts of chemistry and geochemistry at the time the above-identified application and the provisional application (from which the above-identified application claims priority) were filed.

6. I am a shareholder (less than 5% of the outstanding stock), Chairman of the Board of Directors, and a part-time employee of ADA Environmental Solutions, Inc., which wholly owns ADA Environmental Solutions, LLC, the assignee of the above application. I am not an inventor of the above application.

7. In connection with the Office Action mailed January 29, 2004, I reviewed the following documents: (a) the Office Action; (b) U.S. Patent 6,484,651 to Shepard, Jr., et al. (“the Shepard Patent”); (c) the above application (“the Subject Application”); and (d) U.S. Provisional Application Serial No. 60/213,915, filed June 26, 2000, entitled “Low-Cost Technology to Improve Operation of Cyclone Furnaces Firing Low-Sulfur Western Coals” (“Provisional Application”) from which the Subject Application claims priority.

8. At the outset, it is important to understand that, in certain embodiments, the Provisional Application, Subject Application, and Shepard Patent are directed to the same invention. They each disclose the combustion of the same fuel in the same type of combustion chamber in the presence of the same iron-bearing material additive under the same temperature regime. The fuel is a low sulfur western or eastern coal (*see, e.g.*, Provisional Application at pages 1 and 3; Subject Application at Figure 2, page 2, lines 15-17, page 3, lines 9-12, page 4, lines 3-4 and 7-9, and page 6, lines 4-5; and Shepard Patent at col. 1, line 62-col. 2, line 3, col. 3, lines 26-34 and 55-57 and Fuels 3 and 4). The combustion chamber is a “slag tap” or “wet bottom” boiler, such as a cyclone-type boiler (*see, e.g.*, Provisional Application at pages 1-5 and 7-8; Subject Application at Figure 1, page 1, lines 18-26, page 5, lines 16-17, page 6, lines 4-5 and 15-18, and page 18, lines 12-13; and Shepard Patent at col. 2, lines 7-8, col. 4, lines 7-10). The iron-bearing material is mill scale from steel production or dust from blast furnace gas cleaning equipment (*see, e.g.*, Provisional Application at pages 4 and 6; Subject Application at page 12, lines 7-12; and Shepard Patent at col. 4, lines 15-16, col. 8, lines 4-5). The temperature regime is that necessary to combust the solid fuel and melt the ash content of the fuel to form slag. (*see, e.g.*, Provisional Application at pages 1-5 and 7-8; Subject Application at page 2, lines 14-15, page 6, lines 4-5 and lines 15-18, Figures 7-8 and page 20, lines 1-21; and Shepard Patent at col. 2, lines 4-50, col. 5, lines 10-50). In chemistry, it is elementary that the use of the same reactants under the same reaction conditions in the same reactor will produce the same results. Thus, the various claim limitations discussed below are inherent in the disclosures of the Provisional and Subject Applications.

9. At page 3 of the Office Action, the Examiner states that the carbon compound limitation of claim 1 of the Subject Application, namely that “at least one carbon compound promoting reduction of iron oxides” be introduced along with the iron-bearing material, fails to comply with the written description requirement of 35 U.S.C. § 112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to

reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

10. I disagree. Although the Shepard patent fails to identify the precise carbon compound(s) referenced by this phrase, it states at col. 8, lines 13-16, that “[c]arbon may be present in the iron-bearing materials in the form of, for example, blast furnace flue dust, or carbon may be added to these materials to promote reduction of the iron oxides to more readily flux the fuel ash.” From this sentence, it is my understanding that the carbon referenced in the Shepard patent is in the form of elemental carbon, coke, and/or hydrocarbons. The Subject and Provisional Applications each reference a number of carbon compounds that would be understood by one of ordinary skill in the art to promote reduction of iron oxides, such as hematite, magnetite, and wustite, under the thermal conditions of the combustion chamber. These compounds include hydrocarbons in the coal feed itself (Provisional Application at page 7 and Subject Application at page 6, lines 6-14); oils and greases (Provisional Application at page 4 and Subject Application at page 12, lines 14-17); xanthum gum (Provisional Application at page 6 and Subject Application at page 13, lines 10-13); and residual hydrocarbons remaining in the boiler slag, which may be added to the iron-bearing material as a flow aid (Provisional Application at page 8 and Subject Application at page 15, lines 1-2). Moreover, as admitted in part by the Shepard patent, iron-oxide reducing carbon compound(s) will be inherently present in the iron-bearing material itself when the iron-bearing material is a byproduct of steel and iron manufacturing, such as Basic Oxygen Furnace or BOF flue dust or precipitator fines, blast furnace flue dust, electric arc furnace dust, and mill scale fines (Provisional Application at page 4 and Subject Application at page 12, lines 7-12, and page 18, lines 13-14).

11. For these reasons, one of ordinary skill in the art, based on the Specifications of the Subject and Provisional Applications, would conclude that, at the time each application was filed, the inventors had possession of an iron-containing additive containing at least one carbon compound to promote reduction of iron oxides in the iron-containing additive.



12. At pages 3 and 5 of the Office Action, the Examiner states that the Ash Fusion Temperature or AFT-characteristic limitation of claims 1, 19, and 24 of the Subject Application, namely that an ash slag produced by combusting the solid fuel in the presence of the iron-bearing material has “at least one ash fusion temperature characteristic selected from the group consisting of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature is less than the same ash fusion temperature characteristic of a second ash slag produced from combustion of the solid fuel alone”, fails to comply with the written description requirement of 35 U.S.C. § 112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

13. I disagree. The Subject and Provisional Applications each state that the iron-bearing additive fluxes the ash (Provisional Application at pages 3-4, 5, and 7 and Subject Application at page 5, lines 13-14, page 6, lines 19-22, page 8, lines 10-11) and lowers the melting temperature of the ash (Provisional Application at page 1 and Subject Application at page 7, lines 15-18, Figures 7-8, and page 20, lines 1-21). The AFT characteristics of initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature represent a continuum of constituent melting points leading to the complete melting of the ash. The characteristics are arbitrary and established by subjective visual observation.

14. According to pages 20-5 through 20-7 of “*Steam/its generation and use*”, by Babcock & Wilcox (1972) (“the Babcock & Wilcox Article” attached hereto as Exhibit “A”), the AFT properties are determined as part of the ASTM Standard D 1857, *Fusibility of Coal and Coke Ash*. According to the standard, an ash sample is prepared by burning coal under oxidizing conditions at temperatures of 1470 to 1650°F. The ash is pressed into a mold to form a triangular pyramid cone 0.75 in. in height with a 0.25 in. triangular base. The cone is heated in a furnace at a controlled rate to provide a temperature increase of 15°F per minute. The initial

deformation temperature (IT or ID) refers to the temperature at which the tip of the pyramid begins to fuse or show signs of deformation. The softening temperature (ST) is the temperature at which the sample has deformed to a spherical shape where the height of the cone is equal to the width at the base ( $H=W$ ). The softening temperature is commonly referred to as the fusion temperature. The hemispherical temperature (HT) is the temperature at which the cone has fused down to a hemispherical lump and the height equals one half the width of the base ( $H=1/2W$ ). The fluid temperature (FT) is the temperature at which the ash cone has melted to a nearly flat layer with a maximum height of 0.0625 in.

15. It is well known that each of the AFT characteristics, namely IT, ST, HT, and FT, represent a melting point of one or more ash constituents. Regarding the relationship between the AFT properties and the melting point of the ash, the Babcock & Wilcox Article states:

The gradual deformation of the ash cone is generally considered to result from differences in melting characteristics of the various ash constituents. As the temperature of the sample is increased, compounds with lowest melting temperature begin to melt, causing the initial deformation. As the temperature continues to increase, more of the compounds melt and the degree of deformation proceeds to the softening and hemispherical stages. The process continues until the temperature is higher than the melting point of most of the ash constituents and the fluid stage is reached.

(The Babcock & Wilcox Article at page 20-6.)

16. For at least these reasons at the times that the Subject and Provisional Applications were filed, one of ordinary skill in the art would understand the phrase, "melting temperature of the ash" (as used in the Subject and Provisional Applications), to refer to the last (or highest) of a sequence of melting points for differing ash constituents and require that each of the lower melting point constituents have melted. The melting temperature of the ash is therefore synonymous with the fluid temperature.

17. Regarding the AFT-characteristic limitation and the fluxing limitation, namely that the “iron bearing material fluxes the ash slag” in claims 1, 11, 19, 24 and 33 (see Office Action at pages 3, 4, 5, and 33), the Provisional and Subject Applications further use the term “flux” and “fluxing agent”. (Provisional Application at pages 1, 3-4, and 6-8 and Subject Application at page 5, lines 13-14, page 6, lines 19-22, page 8, lines 10-11). According to *Hawley's Condensed Chemical Dictionary*, “flux” is defined as “[a] substance that promotes fusing of minerals or metals or prevents the formation of oxides.” It further defines “fuse” as “[o]f a solid, to *melt*, e.g., a fused salt.” (Emphasis supplied.) The terms “flux” and “fuse” would further suggest to one of ordinary skill in the art that the various melting points of the ash constituents, denoted by the AFT properties, are lowered by the iron-bearing additive disclosed in the Provisional and Subject Applications.

18. The Provisional and Subject Applications further refer to the iron-containing additive lowering the  $T_{250}$  (or the temperature at which the ash would have a viscosity of 250 poise and is an important indicator for the minimum temperature at which the slag will flow) for low-sulfur eastern and western coals having low iron and high calcium contents. (Provisional Application at pages 1 and 4-5 and Subject Application at Figure 2, page 2, lines 15-17, page 7, lines 15-18, page 9, lines 14-15, page 19, lines 5-10, Figures 7-8 and page 20, lines 3-21). As shown in Figure 7 of the Subject Application, the iron-containing additive lowers the slag viscosity, at temperatures above about 2275°F, compared to a slag when no additive is used. It is inherent that the use of the iron-bearing material to lower the  $T_{250}$  of low-sulfur coals having low iron and high calcium contents will lower each of the AFT properties referenced above.

19. For at least the reasons set forth above, the AFT-characteristic and fluxing limitations are each described in the Specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that

the inventors, at the time each of the applications was filed, had possession of the claimed invention.

20. Claims 1, 19, and 24 further require the iron-bearing material to cause a reduction in at least one AFT characteristic and ash slag melting point relative to the ash slag in the absence of the iron-bearing material. The Provisional and Subject Applications further refer to the iron-containing additive lowering the  $T_{250}$  (or the temperature at which the ash would have a viscosity of 250 poise and is an important indicator for the minimum temperature at which the slag will flow) for low-sulfur western and eastern coals having low iron and high calcium contents. (Provisional Application at pages 1 and 4-5 and Subject Application at Figure 2, page 2, lines 15-17, page 7, lines 15-18, page 9, lines 14-15, page 19, lines 5-10, Figures 7-8 and page 20, lines 3-21). As shown in Figures 7-8 of the Subject Application, the iron-containing additive lowers the slag viscosity, at temperatures above about 2275°F, compared to a slag when no additive is used. It is inherent that lowering the  $T_{250}$  of low-sulfur coals having low iron and high calcium contents will lower each of the AFT properties referenced above.

21. Finally, at pages 4, 5, and 6 of the Office Action, the Examiner states that the claimed requirements (of claims 3, 17, 22, and 36) that the at least one AFT characteristic or melting point of the composite ash slag be less than 2,600°F fail to comply with the written description requirement of 35 U.S.C. § 112, first paragraph, because the limitation was not described in the specification of the above application in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

22. I disagree. The Provisional Application at page 1 and the Subject Application at page 2, lines 14-15, disclose that the ash (from which the molten slag is formed), in cyclone boilers, must be melted at normal combustion temperatures ranging

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from 2,600 to 3,000°F. Moreover, the Subject Application at page 20 and in Figure 7 shows that the ash/slag is melted at a temperature below 1,900°F.

23. For at least the reasons set forth above, the requirement referenced in ¶21 is described in the Specifications of both the Provisional and Subject Applications in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time each of the applications was filed, had possession of the claimed invention.

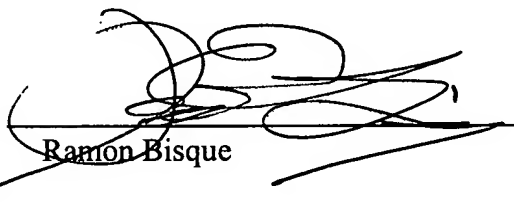
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Respectfully submitted,

Date:

July 29, 2004

By:

  
Ramon Bisque

# Steam / its generation and use

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## Chapter 10

## Cyclone Furnaces

Over the years continuing advances have been made in the methods of burning coal. The introduction of pulverized-coal firing in the 1920's was a major advance, providing advantages over stoker firing as listed in Chapter 9. Today, pulverized-coal firing is highly developed and is still the best way to burn many types of coal, particularly the higher grades and ranks.

However, during the last 35 years, another method of burning coal, the Cyclone Furnace, has been developed and is now widely used. Cyclone-Furnace firing represents the most significant advance in coal firing since the introduction of pulverized coal.

The Cyclone Furnace is applicable to coals having a slag viscosity of 250 poises at 2600F or lower, provided the ash analysis does not indicate excessive formation of iron or iron pyrites (see *Suitability of Fuels for the Cyclone Furnace*). With these coals, Cyclone-Furnace firing provides the benefits obtainable with pulverized-coal firing plus the following advantages:

1. Reduction in fly ash content in the flue gas.
2. Saving in the cost of fuel preparation, since only crushing is required instead of pulverization.
3. Reduction in furnace size.

For further understanding a discussion of the combustion of coal particles may be helpful, particularly if this is considered in the framework of the "three T's" of combustion (Chapter 6) with special emphasis on turbulence (mixing) and time.

When coal is burned in boiler furnaces, the combustion of hydrogen is accomplished without difficulty, but successful combustion of carbon to  $\text{CO}_2$  requires special measures to assure a continuing supply of oxygen in contact with carbon particles as long as they remain unburned. Not only must there be intimate mixing of the coal particles and air; there must also be sufficient turbulence to remove the combustion products as they form at the surface of the fuel and provide fresh air at the fuel surface to continue combustion. The greater the turbulence the more rapid the process; hence less time is required for combustion.

With pulverized-coal firing, the coal is reduced to a powder, so fine that approximately 70 percent will pass a

200-mesh screen. The finely pulverized coal is then very intimately mixed with combustion air in the burner, however, after this initial mixing the tiny coal particles are merely carried along in the air stream, and very little additional scrubbing by the air occurs. Thus, further contact of oxygen with the coal must be largely by diffusion. The furnace consequently has to be relatively large to give the necessary retention time for oxygen to diffuse through the blanketing  $\text{CO}_2$  layer to reach the coal particles and, at the same time, temperatures must be sufficiently high to complete combustion. After combustion, since the residual ash particles are much smaller than even the original tiny pulverized-coal particles, the former are easily carried along with the flue gases from the furnace and through the boiler setting.

At the same time the pulverized-coal-fired boiler furnace also has the function of cooling the combustion

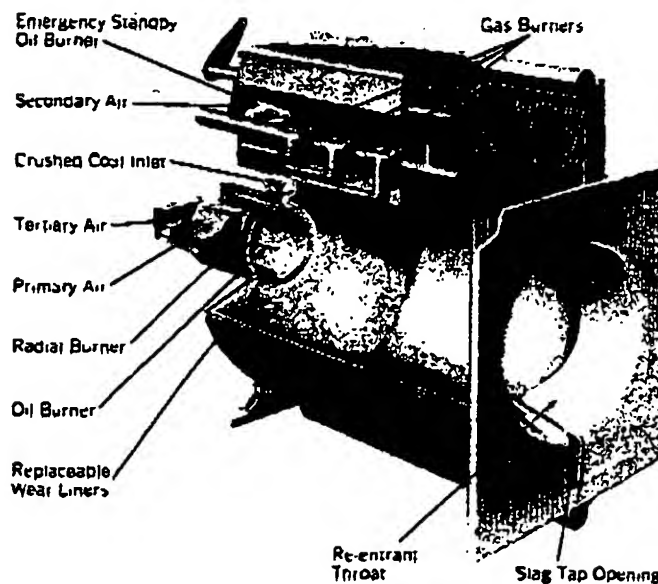


Fig. 1 The Cyclone Furnace, in the form of a horizontal cylinder, is completely water cooled by connection to the main boiler circulation. All combustion gases leave through the re-entrant throat at the rear. Molten slag drains from the bottom at the rear through a small opening into the adjacent boiler furnace.



gases, so that when they enter the convection surfaces they are below the temperature at which slagging occurs. This function conflicts with that of maintaining the high temperatures necessary to complete combustion. It would therefore be advantageous to separate these functions by providing a separate small combustion chamber where high turbulence and temperature may be maintained, and using the main boiler furnace primarily to cool the combustion gases.

For many years engineers recognized this need and actively explored basic changes in the design of furnaces and fuel-burning equipment to improve combustion and furnace performance. In addition, significant changes in availability and use of coal further increased the need for new designs, e.g., demands for higher grades of coal have depleted many seams, and others have been reserved for metallurgical and other uses. Mechanization in coal mining has increased the ash content of mined coal.

Washing is widely used to lower ash and sulfur contents; however, this is an added expense (see Chapter 8). The industrial growth of the Western portion of the country, rich in reserves of subbituminous and lignitic coal, is rapidly increasing the consumption of these lower ranks of coal. This has furthered the need for equipment fully suitable for the lower grades and ranks of high-ash, low-fusion-temperature coal. The Cyclone Furnace is an outgrowth of efforts to meet these needs and to overcome difficulties encountered with other firing methods.

### Principle of operation

The Cyclone Furnace (Fig. 1) is a water-cooled horizontal cylinder in which fuel is fired, heat is released at extremely high rates, and combustion is completed. Its water-cooled surfaces are studded, and covered with refractory over most of their area (see Chapter 16). Coal crushed in a simple crusher, so that approximately 95 percent will pass a 4-mesh screen, is introduced into the burner end of the cyclone. About 20 percent of the combustion air, termed primary air, also enters the burner tangentially and imparts a whirling motion to the incoming coal. Secondary air with a velocity of approximately 300 fps is admitted in the same direction tangentially at the roof of the main barrel of the cyclone and

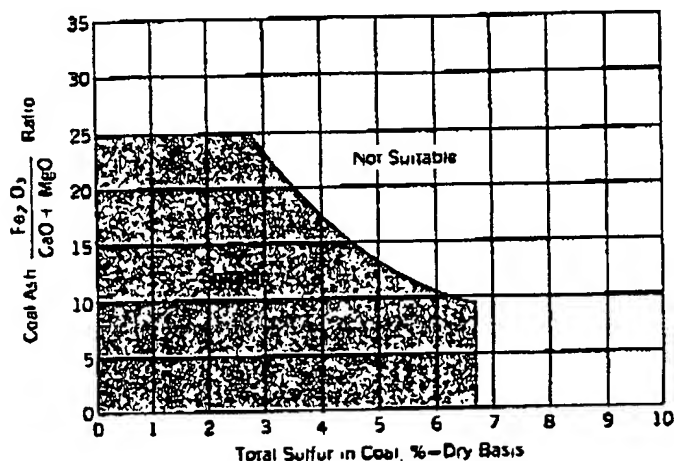


Fig. 2 Coal suitability for Cyclone Furnaces based on tendency to form iron and iron sulfide.

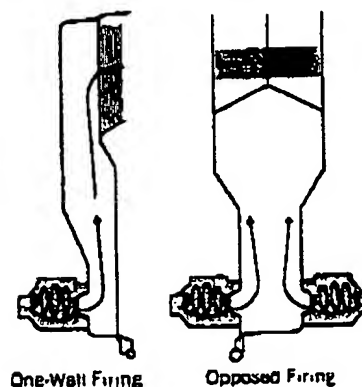


Fig. 3 Firing arrangements used with Cyclone Furnaces.

imparts a further whirling or centrifugal action to the coal particles. A small amount of air (up to about 5%) is admitted at the center of the burner. This is known as "tertiary" air (Fig. 1).

The combustible is burned from the fuel at heat release rates of 450,000 to 800,000 Btu/cu ft, hr, and gas temperatures exceeding 3000F are developed. These temperatures are sufficiently high to melt the ash into a liquid slag, which forms a layer on the walls of the cyclone. The incoming coal particles (except for a few fines that are burned in suspension) are thrown to the walls by centrifugal force, held in the slag, and scrubbed by the high-velocity tangential secondary air. Thus the air required to burn the coal is quickly supplied, and the products of combustion are rapidly removed.

The release of heat per cu ft in the Cyclone Furnace is very high. However, there is only a small amount of surface in the cyclone and this surface is partially insulated by the covering slag layer. Heat absorption rates range from 40,000 to 80,000 Btu/sq ft, hr. This combination of high heat release and low heat absorption assures the high temperatures necessary to complete combustion and to provide the desired liquid slag covering of the surface.

The gaseous products of combustion are discharged through the water-cooled re-entrant throat of the cyclone (Fig. 1) into the gas-cooling boiler furnace. Molten slag in excess of the thin layer retained on the walls continually drains away from the burner end and discharges through the slag tap opening, shown in Fig. 1, to the boiler furnace, from which it is tapped into a slag tank, solidified, and disintegrated for disposal (see *Slag Handling Equipment*).

By this method of combustion the fuel is burned quickly and completely in the small cyclone chamber, and the boiler furnace is used only for cooling the flue gases. Most of the ash is retained as a liquid slag and tapped into the slag tank under the boiler furnace. Thus, the quantity of fly-ash is low and its particle size so fine that erosion of boiler heating surfaces is not experienced even at high gas velocities.

### Suitability of fuels for the Cyclone Furnace

The Cyclone Furnace is capable of burning successfully a large variety of fuels. A wide range of coals varying in rank from low volatile bituminous to lignite may be successfully burned, and in addition other solid fuels such

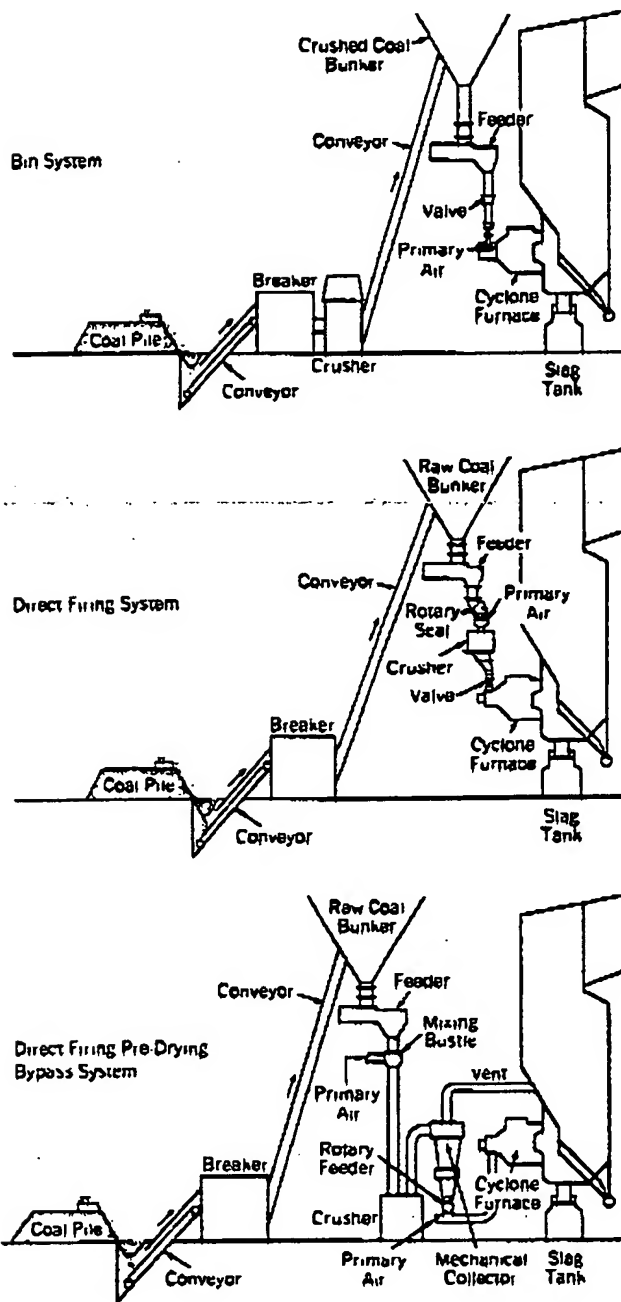


Fig. 4 Bin, direct-firing, and direct-firing pre-drying bypass systems for coal preparation and feeding to the Cyclone Furnace (schematic).

as wood bark, coal chars, and petroleum coke may be satisfactorily fired in combinations with other fossil fuels. Fuel oils and gases are also suitable for firing.

The suitability of coals is dependent on the moisture, ash and volatile contents of the coal together with the chemical composition of the ash. The volatile matter should be higher than 15 percent, on a dry basis, to obtain the required high combustion rate. The ash content should be a minimum of about 8 percent to provide a proper slag coating in the cyclone and can be as high as 25 percent on a dry basis. A wide range of moisture content is permissible depending on coal rank, secondary air temperature and fuel preparation equipment that may include capability for pre-drying the fuel.

One of the two important criteria for coal suitability is the total amount of sulfur compared to the ratio of iron to calcium and magnesium (Fig. 2). This comparison gives an indication of the tendency of the coal to form iron and iron sulfide, both of which are very undesirable in the Cyclone Furnace. Coals with too high sulfur content and/or a high iron ratio are not considered suitable.

The other important criterion for establishing the suitability of coal for firing in the cyclone is the viscosity of the slag formed from the ash. Since satisfactory combustion of coal depends on the formation of a liquid slag layer in the cyclone, and since ash is removed from the cyclone and primary furnace in fluid form, the viscosity of the slag must permit slag flow at the temperatures experienced in the cyclone and primary furnace. Field experience with many different coals together with extensive investigation of ash characteristics has provided information for evaluating coal suitability, from a slag tapping standpoint, without actual firing tests.

Slag will just flow on a horizontal surface at a viscosity of 250 poises. The temperature at which this viscosity occurs ( $T_{250}$ ) is used as the criterion to determine the suitability of a coal from this point of view. The  $T_{250}$  is calculated from a chemical analysis of the coal ash, and a value of 2600F is considered maximum (see *Viscosity of Coal-Ash Slag, Chapter 15*). Somewhat lower temperatures may be desirable for fuels with high moisture contents and low heating values.

The suitability of other solid fuels such as wood, bark, petroleum coke or chars must be considered on an individual basis and the amount of supplementary fuel carefully calculated.

## Design features

### Boiler furnace

The two general firing arrangements used for the Cyclone Furnace are one-wall firing and opposed firing. These are shown in Fig. 3. For smaller units, sufficient firing capacity is usually attained with Cyclone Furnaces located in only one wall. For large units, furnace width can often be reduced by using opposed firing.

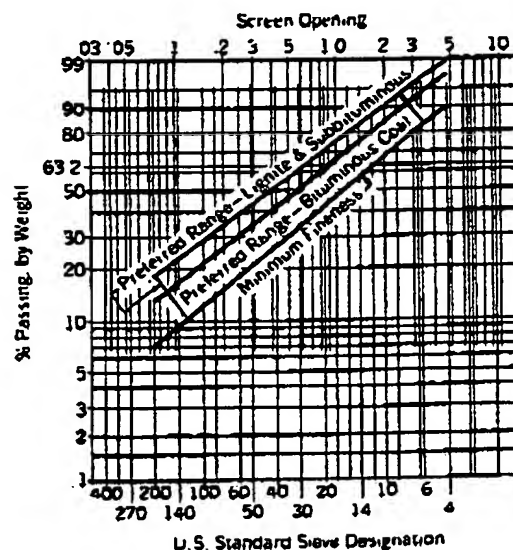


Fig. 5 Sizing of crushed coal fired in the Cyclone Furnace.

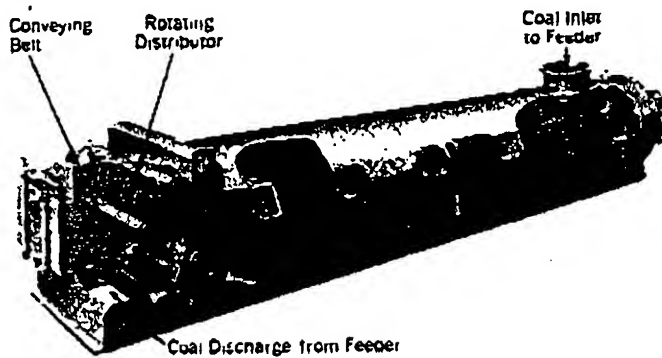


Fig. 6 Belt-type coal feeder for the Cyclone Furnace.

### Cyclone Furnace capacities

The size and number of Cyclone Furnaces used to fire a given boiler depend primarily on the boiler size and the load flexibility required. They are built commercially in sizes ranging from 8 ft diameter through 10 ft diameter, with an allowable maximum heat input per furnace of about 160 million to 425 million Btu/hr, respectively.

### Coal preparation

There are two general types of coal preparation and feeding (see Fig. 4), the bin or storage system and the direct-firing system. The former is preferred for most bituminous coals when the plant layout permits. The range of sizing of crushed coal required with either system is given in Fig. 5.

With the bin system, coal is crushed in a central preparation plant to a size suitable for firing, and the crushed coal is delivered to the bunker. Because the crushed coal is relatively large in particle size, the hazards associated with pulverized-coal systems do not exist. The only precaution necessary is to provide adequate venting of the bunkers to assure removal of the small amounts of combustible gases released from freshly crushed coal of certain types. With the bin system there is less equipment in the boiler room, and short crusher outages can be accommodated without interrupting boiler operation.

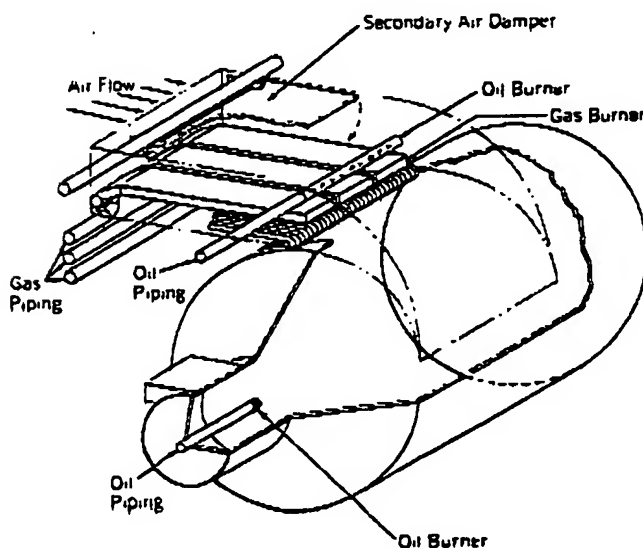


Fig. 7 Arrangement of gas and oil burner in Cyclone Furnace.

The second method of coal preparation is the direct-firing system, which has a separate crusher located between the feeder and the burner of each Cyclone Furnace. The crusher is swept by hot air, and the intimate mixing of coal and hot air in the crusher helps to dry the coal. This improves crusher performance and ignition with high moisture coals. It is often easier to accommodate the direct-firing system in existing plants, where the coal handling equipment cannot readily be adapted to the bin system.

The direct-firing, pre-drying, bypass system (Fig. 4) is a variation of the second method, incorporating a mechanical dust collector between the crusher and the Cyclone Furnace. The collector is vented to the boiler furnace. This system is used when firing extremely high moisture coals. Its advantage is that moisture is removed from the coal during crushing and then vented to the boiler furnace instead of the Cyclone Furnace. This maintains maximum temperature in the cyclone with improved performance and slag tapping characteristics.

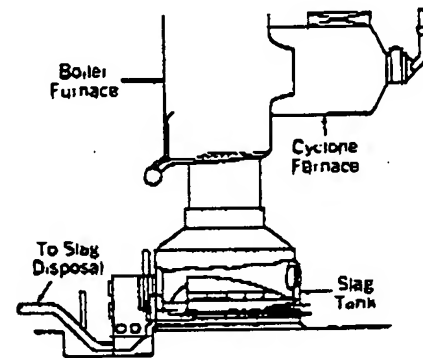


Fig. 8 Batch-removal slag-handling system for Cyclone-Furnace boiler.

### Coal feeders

The coal feeders normally used are of the belt type, illustrated in Fig. 6. A rotating distributor is provided at the coal discharge from the feeder to assure a continuous and uniform rate of feed. This is necessary because the coal is burned almost instantaneously when it reaches the Cyclone Furnace, and fluctuations in feed are reflected in combustion conditions. The rapidity of combustion makes the Cyclone Furnace very responsive to load demands, and it has been demonstrated that boiler output can be made to respond very quickly to demand by changing coal-feeder speed. Continuous weighing devices can be applied to the belt feeder so that it can serve the dual function of coal scale and feeder.

Feeders of other types may also be used. Some are equipped with an angled cutoff plate at the coal discharge from the feeder to provide a uniform rate of feed.

### Oil and gas burners

Oil and gas, as previously noted, are satisfactory cyclone fuels. These fuels can be burned at ratings and with performance equal to those with coal firing. Oil may be injected either into the secondary air stream or through the center of the front coal burner (see Fig. 7), where the oil is picked up and atomized by the high velocity air stream. Gas is fired through flat ports located in the

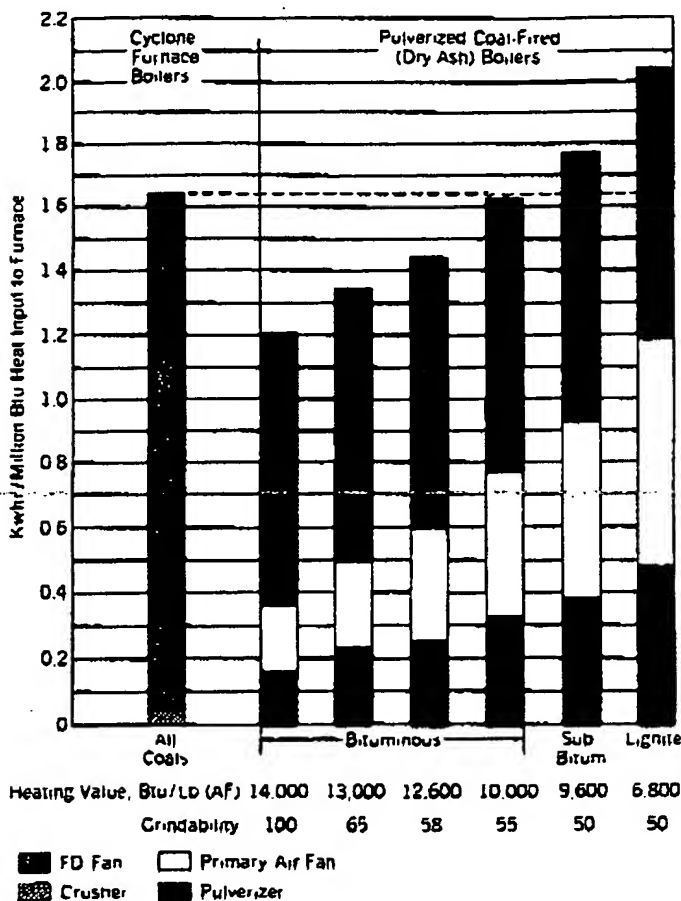


Fig. 9 Auxiliary power requirements of typical high-capacity pressure-fired Cyclone-Furnace and pulverized-coal units.

secondary air entrance to the cyclone. The gas burners and the oil burners located in the secondary air inlet may be left in place when coal is fired. This facilitates changing from one fuel to another by remote control without removal of the Cyclone Furnace from service. This feature makes the Cyclone Furnace most attractive for the firing of multiple fuels. However Cyclone Furnaces are not normally competitive with other firing methods unless coal is to be a principal fuel (see *Cyclone-Furnace Firing, Chapter 22*).

#### Slag handling equipment

Slag handling equipment for a Cyclone-Furnace boiler unit is similar to that for a pulverized-coal slag-tap unit. The capacity of the slag-handling equipment must be greater since the percentage of ash recovered in the Cyclone Furnace is higher. The batch-removal system, illustrated in Fig. 8, is the system generally used. Storage tanks into which slag is continuously tapped, quenched and accumulated are located under the furnace floor. Slag is withdrawn at intervals and discharged to a storage area, from which it may be removed at will (see *Design and Operation of Slag-Tap Units, Chapter 15*).

#### Combustion controls

Automatic combustion controls for Cyclone-Furnace boilers are generally based on maintaining equal coal weights and equal total air flows in the proper proportion to each Cyclone Furnace. Where volumetric type

feeders are used, equal coal weights are obtained by maintaining equal feeder speeds. Where gravimetric type feeders are used, they measure and control the coal weights to the Cyclone Furnaces.

Combustion air flow is measured separately to each cyclone. Where individual ducts supply combustion air to individual cyclones, a venturi throat in each duct measures the air to each cyclone. Where cyclones are installed in a common windbox, secondary air flow is measured at the bell-mouth section of the secondary air port of each cyclone, then added to the primary and tertiary air flows of that cyclone. These flows are measured at orifices in the individual ducts.

Using these measurements, the controls maintain equal coal rates and air flows to each Cyclone Furnace. The overall excess air is controlled in the usual manner with a boiler meter based on steam flow and air flow. Oxygen recorders are usually provided as operating guides to monitor the controls.

### Operating results

#### Fuels burned

The first commercial Cyclone-Furnace boiler was designed to burn Central Illinois coal and was installed at the Calumet Station of the Commonwealth Edison Company, Chicago, in 1944. Since then over 600 Cyclone-Furnace units have been installed in boilers throughout the United States and Europe. In this country coals of the following constituent range have been burned in commercial Cyclone-Furnace boilers:

Moisture, %	2 to 40
Volatile matter (dry), %	18 to 45
Fixed carbon (dry), %	35 to 75
Ash (dry), %	4 to 25

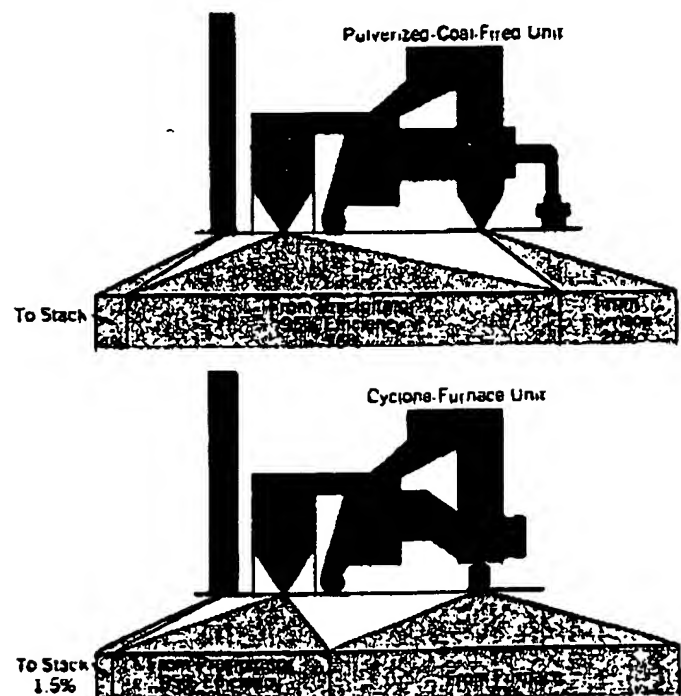


Fig. 10 Comparison of fly-ash emission from typical large dry-ash-removal pulverized-coal-fired unit and Cyclone-Furnace unit.

As mentioned previously, a number of by-products from petroleum and many waste fuels, such as bark, can be successfully burned. The petroleum products range in volatile matter from 5% for some petroleum coke to 60% for pitch. Because of the very low ash content of these petroleum by-products, it is usually necessary to add a slag-forming material or to mix the pitch with a coal having suitable ash characteristics to provide the necessary slag coating of the cyclone barrel. It may also be necessary to stabilize ignition of the low volatile coke by burning 5 to 10% auxiliary oil or gas.

Coal chars, resulting from the low-temperature carbonization of bituminous or lignitic coals having sufficient ash and volatile matter, are suitable for firing, provided the ash viscosity characteristics are suitable.

Two units designed to burn bark and bituminous coal in amounts up to approximately 50% by weight of each are in operation in a large Southern paper mill. To burn the bark successfully, it is necessary to fire sufficient coal to supply the slag coating in the cyclone and to maintain sufficiently high temperatures to provide the necessary fluidity of the slag. A chopper, or "hog", is used to reduce the bark to chips of a size suitable to the Cyclone Furnace. The chips are screened after "hogging" and oversize pieces are recycled.

#### Power requirements

Since the only coal preparation is crushing, the power required is low compared with that for pulverizing coal. To offset this, the forced draft fan power required is relatively high, Cyclone Furnace air pressure drop being in the range of 20 to 40 in. of water compared with 2 to

10 in. of water for pulverized-coal burners. Fig. 9 shows that the comparative power requirements vary considerably for different types of bituminous coals and lignite. For high-heating value, high-grindability bituminous coals, the Cyclone Furnace requires more power. However, for the low-heating value, low-grindability bituminous and lignite coals, for which the Cyclone Furnace is usually best suited, the power requirements are less than with pulverized-coal firing.

#### Combustion efficiency

The excess air required for satisfactory combustion of an individual Cyclone Furnace is less than 10 percent. However, where automatic controls are used and particularly where there are several Cyclone Furnaces for one boiler, excess air is usually maintained between 10 and 15% to assure that no individual cyclone is operating with insufficient air. When operating with coal of suitable sizing and with 10 percent excess air, the loss in efficiency from unburned combustible has been found to be less than 0.1 percent with most coals.

#### Ash recovery and dust collectors

The dust loading of the flue gas from coal-fired cyclone units is in the range of 20 to 30 percent of the ash in the coal, compared with about 80 percent for a dry-ash pulverized-coal-fired unit. This means that, if both units are equipped with 95 percent efficient precipitators or dust collectors, the ash discharged from the stack of a cyclone-fired unit will be less than half that from the stack of a dry-ash pulverized-coal-fired unit.

This comparison is illustrated in Fig. 10 for a large utility Cyclone-Furnace unit and a pulverized-coal unit arranged for dry ash removal. Both units are 600-megawatt capacity, each consuming approximately 7,000 tons of coal per day and producing 970 tons of ash. With pulverized-coal firing about 4 percent of the ash or 39 tons per day is discharged from the stack. Under similar operating conditions with the Cyclone-Furnace-fired unit only approximately 1.5 percent of the ash or 15 tons per day is discharged from the stack. On a Cyclone-Furnace-fired unit the fly ash collected in the precipitator may be returned to the Cyclone Furnace and recovered as slag. The slag from the furnace is chemically inert and disposal is relatively simple.

#### Typical Installations

Although Cyclone-Furnace units were first installed in central stations, their use has been extended to a wide variety of industries. Fig. 11 shows a unit installed in a large Northern industrial plant. The unit incorporates the bin system with one-wall firing. It is designed to produce 440,000 lb/hr of steam at 1350 psi and 905F superheat.

The designs of Cyclone-Furnace units have followed the general trend of the power industry to higher steam temperatures and pressures and larger capacities. Fig. 12 shows a Radiant boiler with one-wall firing. This unit produces 1,250,000 lb/hr of steam at 1900 psi and 1005F, with reheat to 1005F. Fig. 13 shows a Universal-Pressure once-through unit with opposed Cyclone-Furnace firing; the capacity of this unit is 8,000,000 lb of steam per hr at 3650 psi and 1003F, with 1003F reheat temperature.

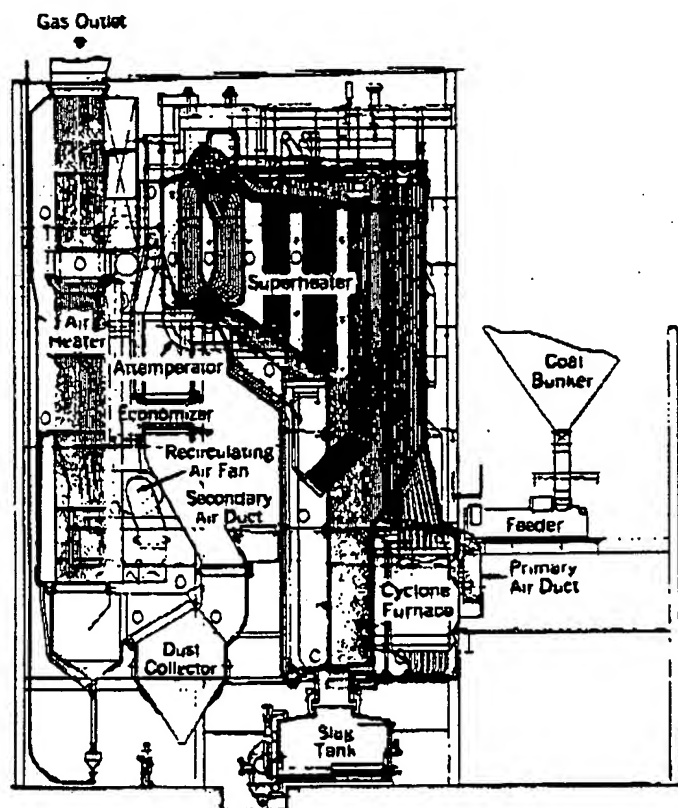


Fig. 11 Two-drum boiler with Cyclone Furnaces (one-wall) and bin system for coal preparation and feeding.



## Operation

### Start-up

The Cyclone Furnace can be started by the continuous firing of coal, oil or gas. Coal is ignited by a permanently installed gas-lighting torch or a retractable oil-lighting torch inserted into the front of the secondary air port. With coal firing, the usual load range for good operation of an individual furnace is from 50 to 100% of rated capacity, depending on the ash characteristics; however, for short periods, such as start-up, loads of 20 to 25% can be carried with some increase in unburned combustible. The load range for continuous operation of the entire Cyclone-Furnace unit is from full to approximately half load, again depending on the ash characteristics and the furnace arrangement. For short periods such as overnight load drops, lower ratings can be carried by allowing the

slag tapped from the Cyclone Furnace to accumulate and solidify on the boiler furnace floor. When the load is increased, this slag will melt and tap in the usual manner.

### Maintenance

The principal items requiring maintenance are the coal crusher and the Cyclone-Furnace burner. Crusher maintenance includes replacement of hammers and grid bars at yearly or less frequent intervals, depending on the arrangement and the type of coal fired. In the burner, the coal is accelerated to the high velocity necessary to throw it against the slagged surfaces of the cyclone barrel. This high velocity causes erosion of the burner, which is minimized by the use of tungsten carbide or other erosion-resistant wear liners (Fig. 14). Since these liners normally last a year or more, they can be replaced or built up during regularly scheduled annual outages.

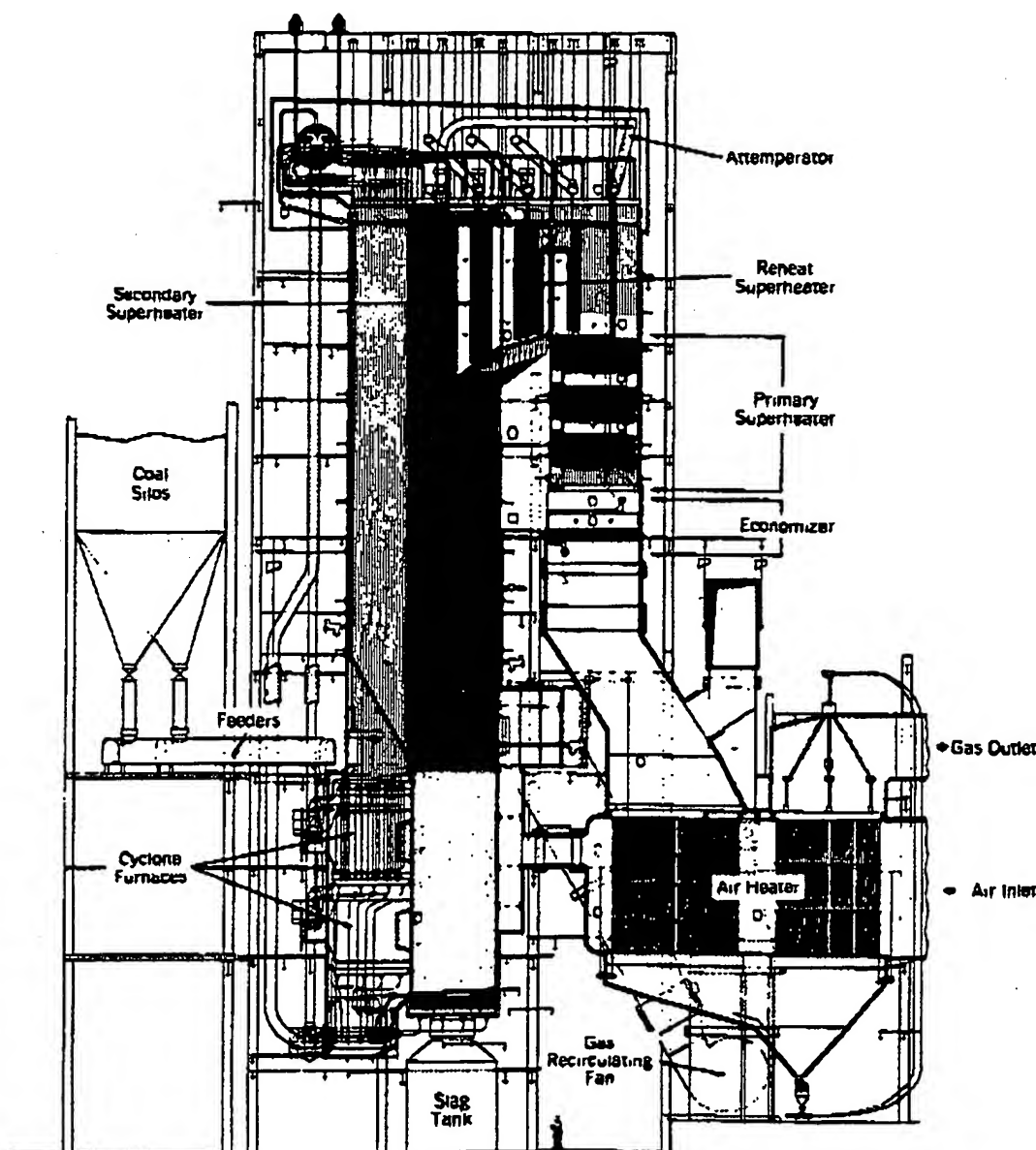


Fig. 12 Radiant boiler with Cyclone Furnaces (one-wall) and bin system for coal preparation and feeding.

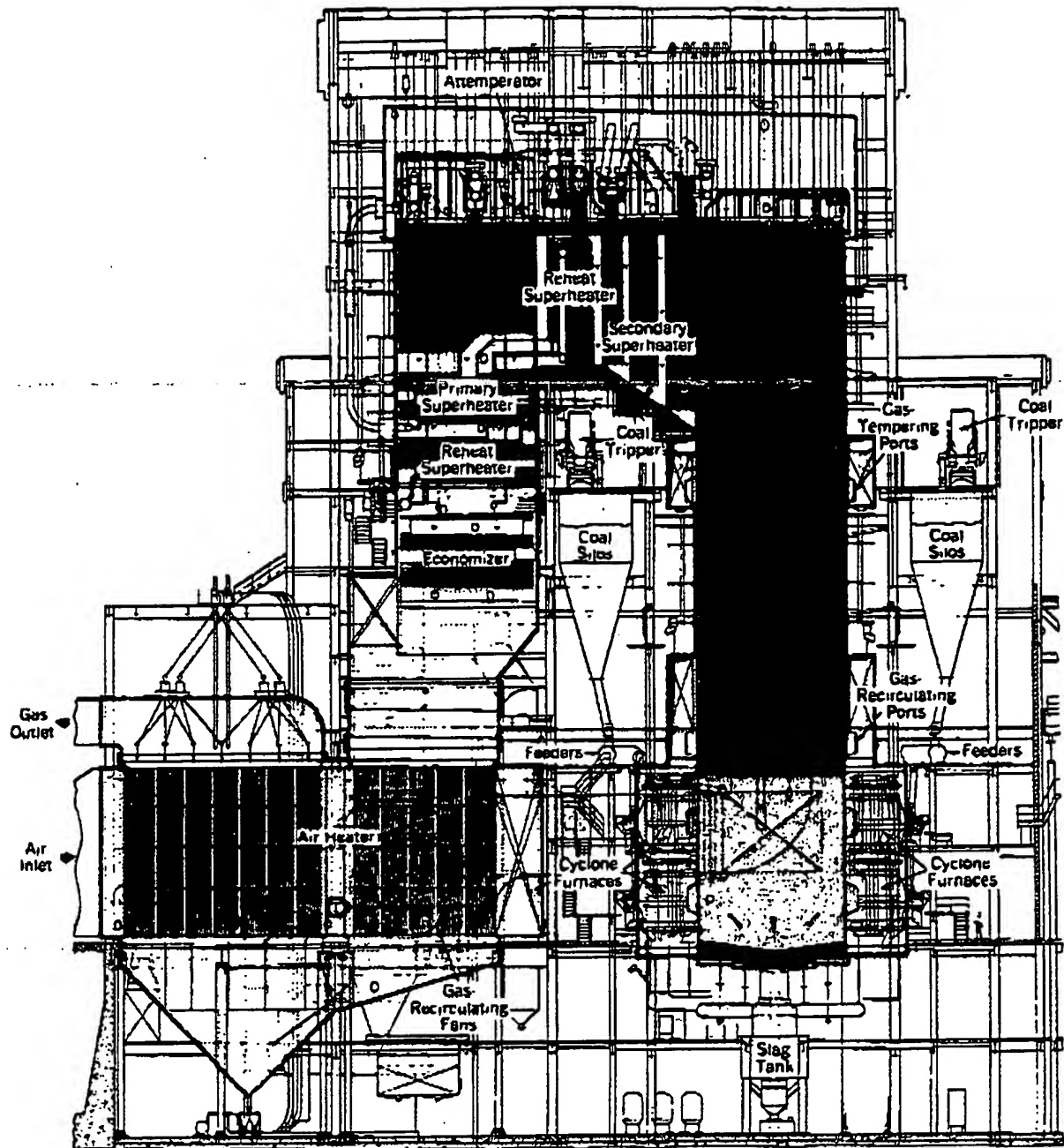


Fig. 13 Universal-Pressure boiler with opposed Cyclone Furnaces and bin system for coal preparation and feeding.

### Summary

The Cyclone Furnace has made a significant contribution to the steam-power industry by improving combustion and furnace performance, by permitting the economic utilization of the lower grades and ranks of coal, and by alleviating the problems caused by coal ash. Because of this, it has gained wide acceptance in the U.S. and abroad. By 1970 about 700 Cyclone Furnaces were in service, under construction or on order for installation in the United States. These Cyclone Furnaces serve more than 150 boilers with a combined capacity of more than 200 million lb of steam per hr.

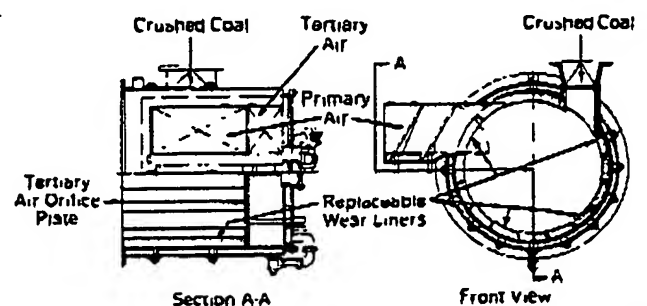


Fig. 14 Burner of Cyclone Furnace showing replaceable wear liners.

## Chapter 15 Fuel-ash effects on boiler design and operation

From the beginning of the application of combustion of fossil fuels for the production of power, much attention has been devoted to the problems created by the residues of such combustion, broadly known as "ash." The complexity of these problems has increased with the size and rating of modern units. When burned, all but a few fuels have solid residues, and in some instances the quantity is considerable.

For continuous operation, removal of ash is essential to all methods of firing. In stoker firing with a fuel bed this is accomplished by the intermittent shaking or dumping of grate sections or by the continuous movement of the ash residue toward a point of discharge. In suspension firing the ash particles are carried out of the furnace by the gas stream or retained in part by settling or by adhering to boiler surfaces. Retained material of solid form is removed by periodic cleaning. If temperatures are sufficiently high, the retained ash is molten and may be drained continuously from the furnace. Some of the ash may form deposits of slag on the furnace walls (slagging), and a portion of the ash that is carried from the furnace by the flue gases may form deposits on the tubes in the gas passes (fouling). Also, under some conditions, the deposits may lead to corrosion of these surfaces. The nature and the amount of ash in the fuel to be used are, therefore, of major concern to the designer and the operator.

The following discussion is concerned primarily with the importance of coal ash in the design and operation of boilers, but consideration is also given to the importance of ash residue from petroleum fuels. Commercial fuels containing ash, and others with little or no ash, are listed in Table 1.

Some means must be provided to handle and dispose of the ash since ash in its various forms may seriously interfere with operation or even cause shutdown.

### Ash content of coal

The ash content of coals varies over a wide range. This variation occurs not only in coal from different parts of the world or from different seams in the same region but also in coal from different parts of the same mine. Some rock and earthy materials find their way into the mined

product. Before marketing, some commercial coals are cleaned or washed to remove a portion of what would be reported as ash in laboratory determinations (*see Chapter 8*). In any case, the ash determinations of significance to the user are those made at the point of use, and the values noted below are on that basis.

The bulk of bituminous coal used for power generation in the U.S. has an ash content within the range of 6 to 20%. Low values of 3 or 4% are encountered infrequently, and such coals find other commercial uses, particularly in the metallurgical field. On the other hand, some coals may have an ash content as high as 30%. Many high-ash fuels are successfully burned in the Cyclone Furnace as well as in pulverized-coal-fired units. Their use is increasing in localities where the fuel costs indicate a favorable overall economy.

### Nature of coal ash

The presence of ash is accounted for by minerals associated with initial vegetal growth or those which entered the coal seam from external sources during or after the period of coal formation. Appreciable quantities of inorganic material may be contributed to the commercial fuel by partial inclusion of adjacent rock strata in the process of mining.

Since quantitative evaluation of mineral forms is extremely difficult, the composition of the coal ash is

Table 1  
Commercial fuels for power production

Fuels Containing Ash	Fuels Containing Little or No Ash
All coals	Natural gas
Fuel oil—"Bunker C"	Manufactured gas
Refinery sludge	Coke-oven gas (clean)
Tank residues	Refinery gas
Refinery coke	Distillates (most)
Most tars	
Wood and wood products	
Other vegetational products	
Waste-heat gases (most)	
Blast-furnace gas	
Cement-kiln gases	



**Table 2**  
**Ash content and ash fusion temperatures of some U.S. coals and lignite**

Rank:	Low Volatile Bituminous	High Volatile Bituminous				Sub-bituminous	Lignite
Seam	Pocahontas No. 3	No. 9	Pittsburgh	No. 6			
Location	West Virginia	Ohio	West Virginia	Illinois	Utah	Wyoming	Texas
Ash, dry basis, %	12.3	14.10	10.87	17.36	6.6	6.6	12.8
Sulfur, dry basis, %	0.7	3.30	3.53	4.17	0.5	1.0	1.1
Analysis of ash, % by wt							
SiO <sub>2</sub>	60.0	47.27	37.64	47.52	48.0	24.0	41.8
Al <sub>2</sub> O <sub>3</sub>	30.0	22.96	20.11	17.87	11.5	20.0	13.6
TiO <sub>2</sub>	1.6	1.00	0.81	0.78	0.6	0.7	1.5
Fe <sub>2</sub> O <sub>3</sub>	4.0	22.81	29.28	20.13	7.0	11.0	6.6
CaO	0.6	1.30	4.25	5.75	25.0	25.0	17.5
MgO	0.6	0.85	1.25	1.02	4.0	4.0	2.5
Na <sub>2</sub> O	0.5	0.28	0.80	0.36	1.2	0.2	0.6
K <sub>2</sub> O	1.5	1.97	1.60	1.77	0.2	0.5	0.1
Total	98.8	98.44	95.74	95.20	97.5	86.4	84.3
Ash fusibility							
Initial deformation temperature, F							
Reducing	2900+	2030	2030	2000	2060	1990	1975
Oxidizing	2900+	2420	2265	2300	2120	2190	2070
Softening temperature, F							
Reducing		2450	2175	2160		2180	2130
Oxidizing		2605	2385	2430		2220	2190
Hemispherical temperature, F							
Reducing		2480	2225	2180	2140	2250	2150
Oxidizing		2620	2450	2450	2220	2240	2210
Fluid temperature, F							
Reducing		2620	2370	2320	2250	2290	2240
Oxidizing		2670	2540	2610	2460	2300	2290

customarily determined by chemical analysis of the residue produced by burning a sample of coal at a slow rate and at moderate temperature (1350F) under oxidizing conditions in a laboratory furnace. It is thus found to be composed chiefly of compounds of silicon, aluminum, iron, and calcium, with smaller amounts of magnesium, titanium, sodium and potassium. The analyses of coal ash in Table 2 indicate what may be expected of some coals from various areas of the United States. A comparison of analysis of ash from wood and from two low-ash-content lignite coals is indicated in Table 3. The ash analyses do not always total 100%, since the analysis does not include all constituents.

The element sulfur is present in practically all coal, and its effect on equipment performance has been given much attention. Sulfur itself burns as a fuel with a relatively low heating value (3980 Btu/lb when burned to SO<sub>2</sub>), but its reputation, which is nearly all bad, results from the effect of its chemical combination with other elements. Under certain conditions some of these compounds corrode boiler components; others contribute to the fouling and slagging of gas passages and heating surfaces.

Some of the sulfur in coal is in combination with iron as FeS<sub>2</sub>. Sulfur may also be present in the form of complex organic compounds and, in minor amounts, in combination with the alkaline earths (calcium and magne-

sium). When the fuel is burned, the sulfur compounds are normally converted to more or less stable mineral oxides and sulfur dioxide gas, SO<sub>2</sub>. A very small part of the SO<sub>2</sub> thus formed is further oxidized to SO<sub>3</sub>. These sulfur gases are carried along with the other combustion gases, and their presence, under certain conditions, can contribute to corrosion of boiler heating surfaces and to air pollution problems (Chapter 18).

**Table 3**  
**Comparison of ash from two lignites with wood ash**

	Lignite-Type Ash		Wood Ash
Ash, dry basis, %	5.0	6.0	1.0
Sulfur, dry basis, %	1.0	1.0	0.1
Analysis of ash, % by wt*			
SiO <sub>2</sub>	17.9	18.9	33.8
Al <sub>2</sub> O <sub>3</sub>	13.2	18.5	2.6
TiO <sub>2</sub>	0.5	0.6	0.2
Fe <sub>2</sub> O <sub>3</sub>	6.0	6.4	1.6
CaO	59.7	40.8	56.5
MgO	2.0	12.7	4.7
Na <sub>2</sub> O	0.2	1.0	0.5
K <sub>2</sub> O	0.5	0.1	0.1
Total	100.0	100.0	100.0
Ash Fusibility—Hemispherical Temperature, F			
Reducing	2680	2470	2580
Oxidizing	2650	2470	2550

\* Adjusted to 100%

Coals may be classified into two groups based on the nature of their ash constituents. One is the bituminous-type ash and the other is the lignite-type ash. The term "lignite-type" ash is defined as an ash having more CaO plus MgO than  $\text{Fe}_2\text{O}_3$ . By contrast, the "bituminous-type" ash will have more  $\text{Fe}_2\text{O}_3$  than CaO plus MgO.

Locations of U.S. deposits of coals are shown in Fig. 2, Chapter 5. The coal fields labeled "bituminous-type ash" include all those of Triassic age and older coals. The fields shown for "lignite-type ash" include all those of Jurassic age and younger coals, and all ranks of coals in these deposits.

#### Ash fusibility

The preferred procedure for the determination of ash fusion temperatures is outlined in ASTM Standard D-1857. Earlier procedure used only a reducing atmosphere for ash-fusibility determination whereas the standard adopted in 1968 offers the use of both reducing and oxidizing atmospheres. The previous method had loosely defined softening and fluid critical points; the new procedure uses improved definitions, as follows:

**Initial deformation temperature**, at which the first rounding of the apex of the cone occurs.

**Softening temperature**, at which the cone has fused down to a spherical lump in which the height is equal to the width at the base.

**Hemispherical temperature**, at which the cone has fused down to a hemispherical lump at which point the height is one half the width of the base.

**Fluid temperature**, at which the fused mass has spread out in a nearly flat layer with a maximum height of one-sixteenth in.

The determination of ash fusion temperatures is strictly a laboratory procedure, developed in standardized form, which experience shows can be duplicated with some degree of accuracy. For example, the permissible differences of reproducibility between two furnace runs may range from 100 to 150F. However, some bituminous-type ash, containing relatively large amounts of silica, may exhibit low ash-softening temperatures, yet exhibits high viscosity characteristics in its plastic range. Some lignite-type ash, containing large amounts of calcium and magnesium, may react with the refractory base (kaolin and alumina), or it may evolve gaseous products and swell, thereby causing changes in density of the ash cone. Methods for determining fusibility of coal ash used by countries outside the U.S. may also vary considerably. Thus, ash fusibility data should be used with care and its limitations recognized.

Ash melts when heated to a sufficiently high temperature. Following combustion, individual ash particles are generally in the form of tiny spheres (cenospheres) that appear hollow when viewed under a microscope, as illustrated in Fig. 1. The form of the ash particles indicates that, during combustion of the coal, the particles were actually liquid and the spheres were formed as tiny bubbles by evolved gases trying to escape. What happens to these particles depends on their physical and chemical characteristics and on furnace conditions. If

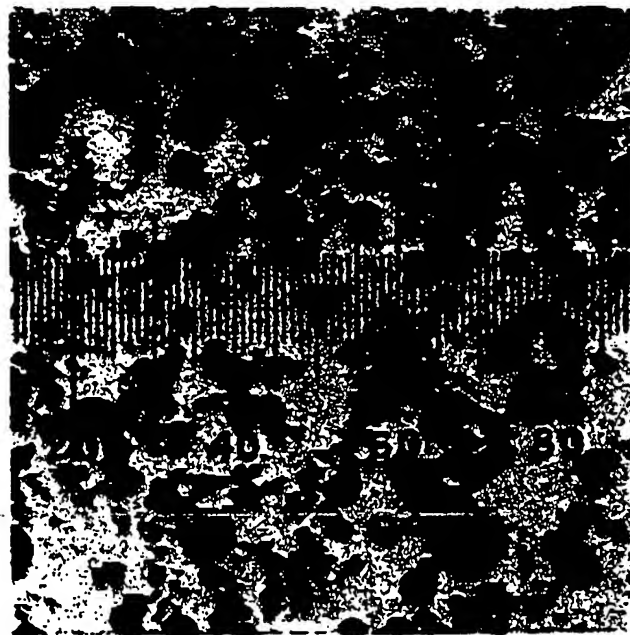


Fig. 1 Ash cenospheres (485x) formed in burning pulverized coal.

cooled promptly and sufficiently, the result is a dusty ash that may travel through the equipment, lodge on heating surfaces, drop out in soot hoppers and along flues, or collect at the base of the stack. Those particles that remain in suspension are carried out with the flue gases to the particulate-removal equipment (Chapter 18) and stack.

The individual ash particles do not, however, always cool quickly to a solid state. If insufficiently cooled, they remain molten or sticky and tend to coalesce into large masses in the boiler furnace or other heat-absorption surfaces. This problem is dealt with by adequate design of burners and furnace arrangement for the fuels to be burned and by proper attention to boiler operation.

#### Viscosity of coal-ash slag

Viscosity of coal-ash slag is measured in a high-temperature rotating-bob viscometer (Figs. 2 and 3), similar to one originally developed by the U.S. Bureau of Mines. The control panel is shown at the left in Fig. 2 and the furnace with its measuring element is at the right. A section through the furnace is shown in Fig. 3. The molten-slag sample is placed in a platinum crucible. There is an optical electronic device for measuring the torsional deflection of the calibrated wire, and the torque is recorded on a chart. Provision is made for controlling the atmosphere within the furnace.

Ash is introduced into the crucible at an elevated temperature (2600-2800F) and held at that temperature until it becomes uniformly fluid and all decomposition gases have been expelled. The temperature is then decreased in predetermined steps, and the viscosity is measured at each temperature.

Measurement of viscosity of coal-ash slags provides reliable data that can be used for determining suitability of coals for use in slag-tap type boilers. Since viscosity measurements require a considerable amount of coal ash that may not be readily available and, in addition,

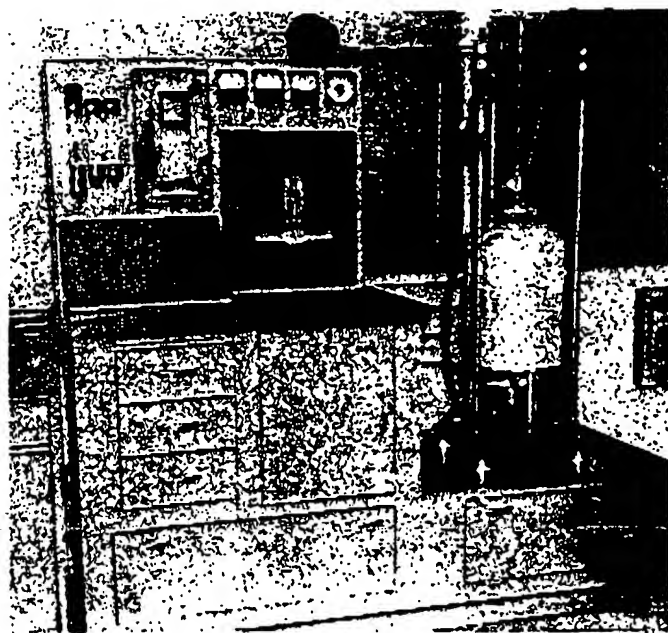


Fig. 2 High-temperature viscometer for determining the viscosity of molten coal ash.

are costly and time consuming, it is desirable to calculate viscosity from chemical analysis of the coal ash. It has been feasible to remove liquid slag from operating furnaces for slags having a viscosity at or below 250 poise. A reasonable temperature limit, to provide ample reduced load operation, has been found to be 2600F. Thus, a dependable guide for suitability of coal-ash slag may be referred to as the  $T_{250}$  or the temperature in degrees F to obtain a 250-poise viscosity.

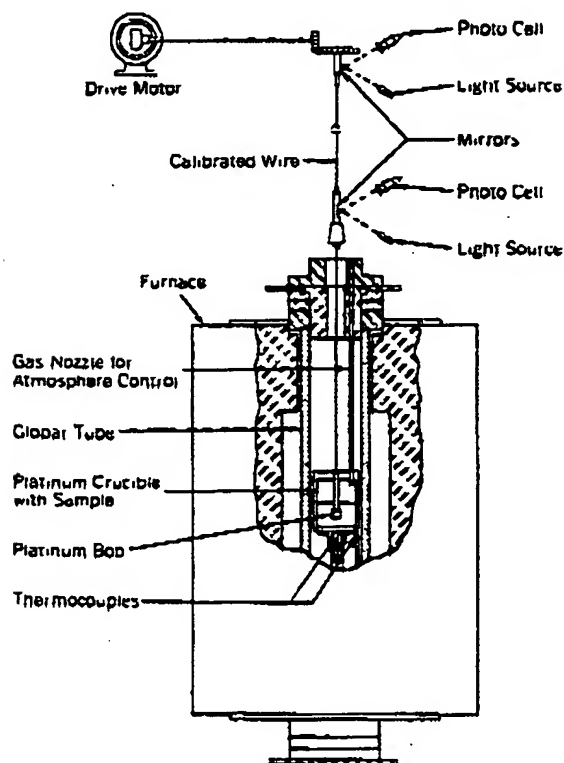


Fig. 3 Section through furnace of high-temperature viscometer.

Laboratory studies and field investigations, supplementing investigations by the Bureau of Mines, resulted in a calculation method for determining the  $T_{250}$  of slag from coals in the eastern United States. This method employs the ash fusibility (hemispherical temperature) in a reducing atmosphere and the "silica ratio" of the coal, where the

$$\text{Silica ratio} = \frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}}$$

The use of this method is illustrated in Fig. 4 where the  $T_{250}$  is obtained by entering with the silica ratio and the hemispherical temperature in a reducing atmosphere plus 200F. For example, for a coal ash having a silica ratio of 62 and a hemispherical temperature of 2300F, locate this point at the intersection of the 2500F line and the 62 silica ratio. From this point extend a straight line at a 10-degree slope from the vertical to the 250-poise value; this slag thus has a calculated  $T_{250}$  of 2450F.

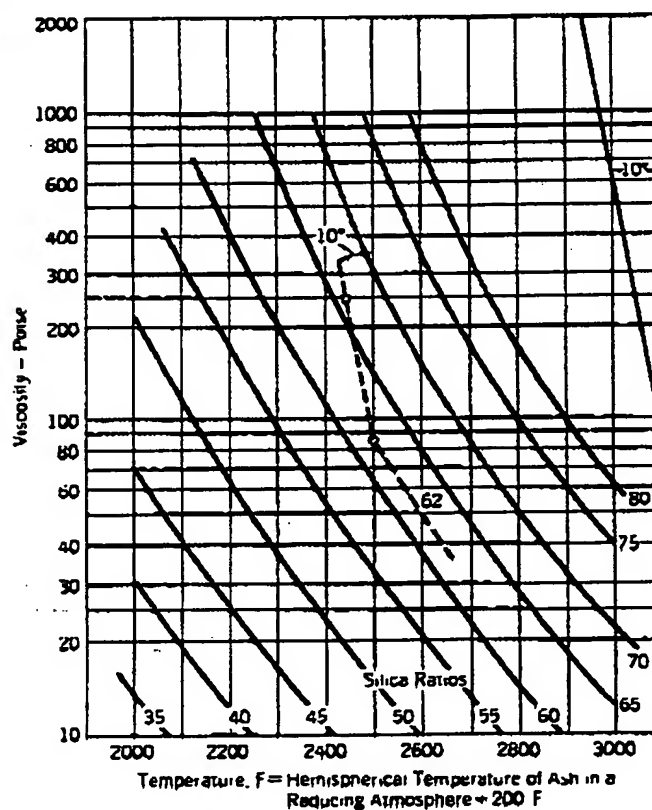


Fig. 4 Slag viscosity from ash analysis.

The constituents of a coal ash can be classed as either basic or acidic. Basic constituents are the  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ ; the acidic constituents are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . Laboratory studies have shown that the relative amounts of the basic and acidic constituents in the ash can be used as a means of predicting the viscosity of the slag (see Fig. 5). The viscosity of a slag decreases as the base-to-acid ratio increases to 1.0 where

$$\text{Base-to-acid ratio} = \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}$$

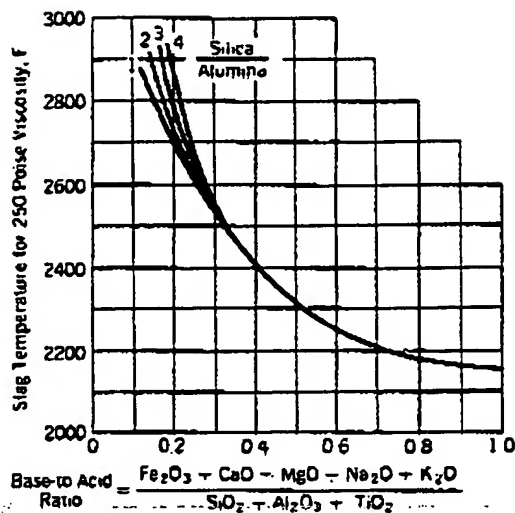


Fig. 5 Plot of temperature for 250-poise viscosity vs base-to-acid ratio—based on a ferric percentage of 20.

This correlation takes into account the  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  ratio which has an effect with slags having a low base-to-acid ratio. For bituminous-type coal ash and for lignite-type ash having an acidic content in excess of 60%, the base-to-acid ratio method is used in preference to the silica-ratio method to estimate the  $T_{250}$ .

For coals with lignite-type ash and an acidic content less than 60%, the dolomite percentage method is used (see Fig. 6).

Dolomite percentage =

$$\frac{(\text{CaO} + \text{MgO})100}{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}$$

where the sum of the basic and acidic constituents is adjusted to equal 100%.

#### Effect of iron on ash behavior

Coals having bituminous-type ash usually contain iron and its compounds as a principal component; the iron may exist in more than one state, i.e., metallic (Fe), ferrous ( $\text{FeO}$ ) or ferric ( $\text{Fe}_2\text{O}_3$ ). The  $\text{Fe}_2\text{O}_3$  reported in an analysis of ash is actually the equivalent  $\text{Fe}_2\text{O}_3$  representing the sum of Fe,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  expressed as  $\text{Fe}_2\text{O}_3$ . Experience indicates that iron has a dominating influence on the behavior of ash in the furnace, as indicated by its effect on the ash softening temperature.

The specific effect of iron in coal ash is interesting. In completely oxidized form ( $\text{Fe}_2\text{O}_3$ ) iron tends to raise all four values of ash fusion temperatures, initial deformation, softening, hemispherical and fluid, while in the lesser oxidized form ( $\text{FeO}$ ) it tends to lower all four of these values. The effect of iron, in each of the two forms, on initial deformation and hemispherical temperatures is indicated in Fig. 7 plotted for a large number of ash samples from U.S. coals. Data in Fig. 7 show that as the amount of iron in the ash increases there is a greater difference in ash fusibility between oxidizing and reducing conditions. This effect may be negligible with coal ash containing small amounts of iron. Lignite-type ash generally contains small amounts of iron and the ash fusion temperatures are affected

very little by the state of oxidation of the iron in the slag. In fact, lignite-type ash having a high basic content and high dolomite percentage may have ash fusion temperatures that are lower on an oxidizing basis than a reducing basis. Ash hemispherical temperatures and ash analyses of lignites appearing in Table 3 illustrate this effect.

The iron content of a slag and the degree of oxidation of the iron also have a great influence on the viscosity of the slag. The degree of iron oxidation is normally expressed as the ferric percentage where

$$\text{Ferric percentage} = \frac{\text{Fe}_2\text{O}_3 \times 100}{\text{Fe}_2\text{O}_3 + 1.11\text{FeO} + 1.43\text{Fe}}$$

In stating the viscosity of a slag containing a significant amount of iron, it is important that the degree of oxidation, or ferric percentage, be expressed. Experience indicates that slags from boiler furnaces operating under normal conditions have an average ferric percentage of 20. The curves appearing in Fig. 5 are based on a ferric percentage of 20. Fig. 8 shows viscosity curves for a typical slag with various stages of oxidation of the iron. For coal ash having small amounts of iron, such as a lignite-type ash, this effect will be greatly diminished.

#### Furnace design

A properly designed furnace has two functions: (1) to burn the fuel completely and (2) to cool the products of combustion sufficiently so that the convection passes of the boiler unit may be maintained in a satisfactory condition of cleanliness, with a reasonable amount of sootblowing (see also Chapter 12). The products of combustion include all the impurities either in the solid, liquid or gaseous state. Experience and tests indicate that when the average gas temperature leaving a coal-fired furnace is too high, the ash particles are molten or

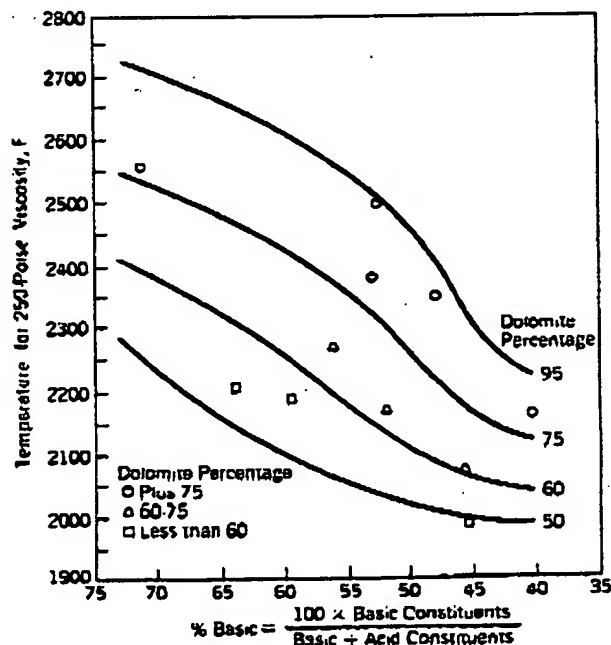


Fig. 6 Basic content and dolomite percentage of ash vs temperature for 250-poise viscosity.

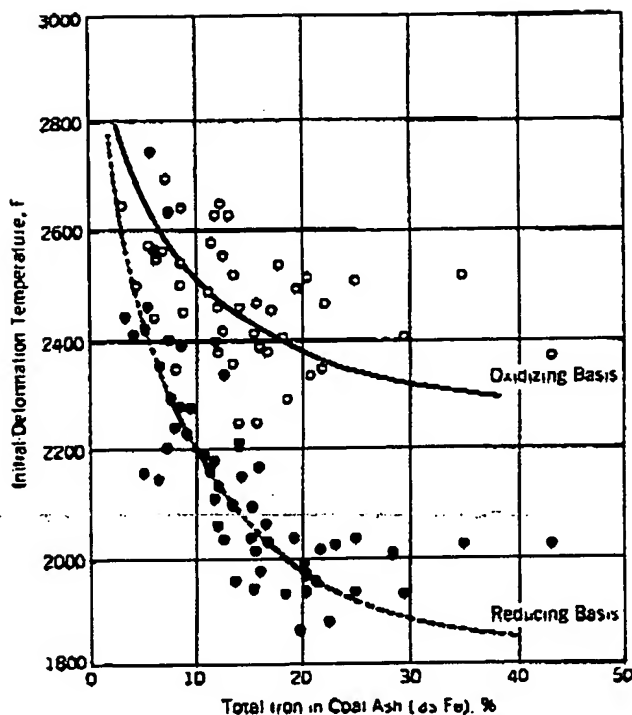


Fig. 7 Influence of iron on coal ash fusion temperatures.

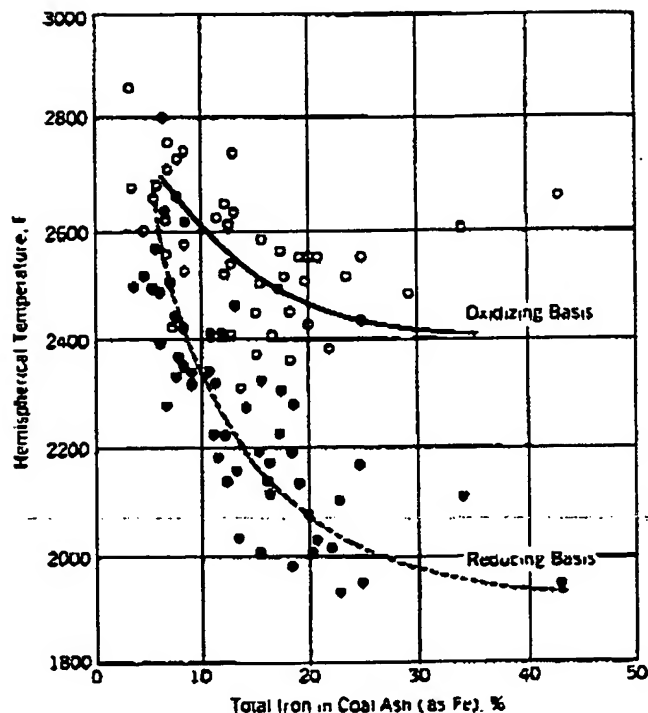


Fig. 8 Viscosity-temperature plots of a typical slag showing effect of ferric percentage.

sticky, and the need for cleaning the ash deposits from the upper-furnace and high-temperature zones in the convection passes may become excessive. This is, of course, subject to some latitude, because what constitutes excessive cleaning depends largely on the opinions of the individual operating crews.

In establishing the proper functional design of a furnace, two methods of cooling the products of combustion must be considered, namely, radiation and gas tempering.

#### Cooling gas by radiation

For many years the method used to cool the products of combustion has been that of providing radiant furnace-cooling surface. Sufficient surface is installed to assure a reduction in gas temperature to a level where convection passes can be kept reasonably clean. There is a general relationship between the average desired furnace-exit-gas temperature and the slagging and fouling potential of the coal ash. There can be a considerable variation in the gas temperature at the furnace outlet (*see Furnaces, Chapter 4*) and the maximum gas temperature can be considerably higher than the average. The usual design criterion of furnace size when using this method of cooling gases is "heat release rate," which is defined as heat available per hour per sq ft of equivalent flat projected water-cooled furnace enclosure surface (*see Chapter 4*).

Heat available, in turn, is defined as the amount of energy released in the furnace and available for increasing the temperature of the products of combustion. It is equal to (heat input in fuel + heat in air) - (heat required to evaporate moisture in fuel +  $\frac{1}{2}$  radiation loss). The assumption that half of the radiation loss occurs from the furnace is an acceptable approximation.

The relationship between furnace release rates and furnace-exit-gas temperatures has been developed from field test data. Factors affecting this relationship include type of furnace design, method of firing, fuel, burner location, burner input, and furnace wall construction.

From information obtained over a number of years, desirable heat release rates have been established for different types of coals. In general, units using coals having low or medium ash-slugging tendencies can have

the highest heat release rates. A boiler designed to burn this type coal is shown in Fig. 9. Units using coals having high or severe ash-slugging tendencies will require furnaces with heat release rates about 10 to 15% lower. Units designed for some very severe ash-slugging coals, such as North Dakota lignites, may require furnace heat release rates reduced by 30% as compared with furnaces designed for low- and medium-slugging-type coals.

With current use of high-volume type train shipments, coal from one source only may be considered for the life of the power plant; it may be shipped, for example, from northern West Virginia to New England. Thus, for best overall operation, units should be designed for the ash characteristics of the coal to be fired.

Furnaces fired with oil are generally designed for high heat release rates. Convection-pass tube spacing can be set in design so as to overcome ash-deposition problems when high-ash oils are fired. With these high heat releases, designs must take into consideration economic factors of tube metals, furnace proportions and high-temperature corrosion.

#### Gas tempering

The second method of cooling hot furnace gas is that known as "gas tempering," in which relatively cool gas from the economizer outlet is mixed with the hot furnace gas near the furnace outlet (Figs. 9 and 10). The tempering gas supply is normally taken from the top of the main gas-recirculation duct. Gas recirculation for superheater control is discussed in Chapter 12.

Gas tempering provides the operator with a control of furnace-exit-gas temperature with little or no effect on superheater and reheater absorption. Thus, if a high-fouling type coal is fired, the amount of tempering gas is increased to lower the gas temperature leaving the furnace to a level at which the convection surface is free from fouling. On the other hand, if a low-fouling type coal is fired, the amount of tempering gas is decreased, thereby reducing fan power. With some coals, tempering may be reduced to zero where experience indicates that it is not needed.

Gas tempering thus provides a positive means of controlling gas temperature at the furnace outlet. With this method of design, furnaces may be held to a reasonable height. Overall building requirements, steam piping, structural steel, and platforms are all decreased with no sacrifice in quality or performance of equipment. Rather, performance has been upgraded, since the gas temperature leaving the furnace is subject to positive control and is not dependent on furnace cleanliness. When gases are cooled only by radiation, the upper furnace cooling surfaces may be covered with slag from low-fouling coal and will not do the required cooling.

With gas tempering, the combustion gases are cooled uniformly across the width of the furnace, minimizing the large temperature variation customary with older designs. The possibility of localized slagging and fouling and excessive superheater-metal temperatures is therefore reduced.

With high steam temperatures and pressures it may be necessary to resort either to steam-cooling the walls or locating steam-cooled surface in high gas-temperature zones in the furnace subject to radiant heat. Gas temper-

ing eliminates these requirements in most cases, and thus improves the reliability and availability of units.

Gas tempering reduces the furnace height required to obtain an equivalent furnace-exit-gas temperature. The Universal-Pressure boiler (Fig. 10), has operated successfully with dry-ash removal with a furnace-exit-gas temperature of 2210F and 20% gas tempering at full load.

Gas tempering permits engineers to design high-capacity units that occupy less space and have greater reliability, lower maintenance, safer operation, and reduced overall plant costs.

#### Ash from pulverized-coal firing

No matter how fine the pulverization, the fuel fed to the furnace still has all its original ash. However, the final ash product ejected from a pulverized-coal-fired unit differs in appearance from the refuse of a stoker-fired unit. With pulverized coal, nearly all the ash particles are formed in suspension and tend to remain in suspension in a dry-ash furnace, with the individual particles well dispersed and very much smaller than those from spreader-stoker firing. In the slag-tap furnace, a portion of the ash particles coalesces on walls or other suitably designed surfaces and drains to the furnace bottom.

When pulverized coal is burned in a dry-ash furnace (e.g., Fig. 10), about 80% of the ash originally in the coal leaves the furnace entrained in the flue gas. On the other hand, with pulverized coal burned in a slag-tap furnace, as much as 50% of the ash may be retained in the furnace. The other 50% of total ash in the coal leaves the unit in the form of dust. With the Cyclone Furnace 70 to 80% of the total ash is retained, and only 20 to 30% leaves the furnace as dry ash in the flue gas (see *Ash Recovery and Dust Collectors*, Chapter 10). Particulate-removal equipment is placed ahead of the stack to prevent the ejection of large quantities of this ash to the atmosphere (Chapter 18).

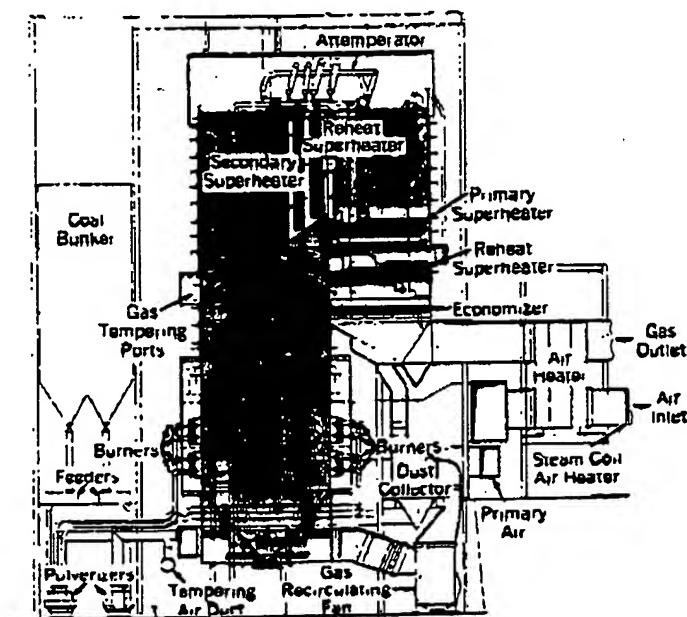


Fig. 9 Universal-Pressure boiler with gas tempering in front wall.



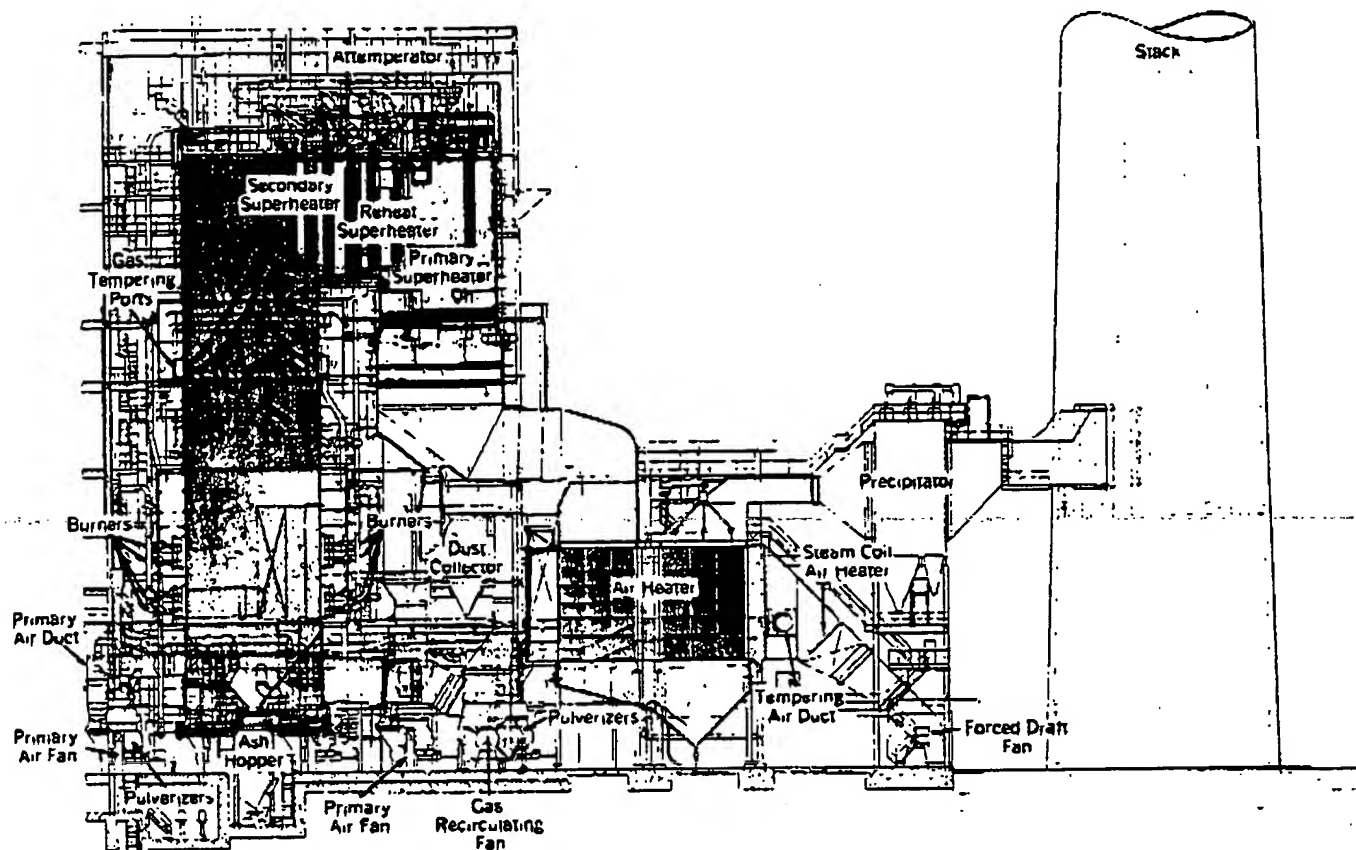


Fig. 10 Universal-Pressure boiler with gas tempering in front and rear walls.

#### Ash produced by stokers

In the fuel bed of a stoker, whether of the spreader, underfeed, or chain-grate type, ash particles tend to become fused together. In a properly operating stoker burning a suitable coal, the passage of air and the agitation of the fuel bed serve to keep ash accumulations more or less porous, and the ash is discharged to an ashpit in fairly large pieces varying from popcorn size upward.

Not all the ash is retained in a fuel bed. With the types of stokers mentioned, and particularly the spreader stoker, some of the fuel is burned in suspension. A considerable quantity of ash particles, containing some unburned and some still-burning fuel, is consequently carried over with the gases. With the spreader stoker this material is usually collected in hoppers provided for the purpose and is reinjected into the furnace for further burning of any combustible that it may contain (see Chapter 11). Rejection is also used occasionally with other types of stokers.

#### Use of dry-ash or slag-tap units

Considered answers to the following pertinent questions relating to fuel are essential in initiating the design of a successful coal-fired unit:

1. Has the particular coal selected been burned extensively, so that its combustion and ash characteristics are well known?
2. Will the source of coal and the characteristics of the

coal remain substantially constant during most of the life of the equipment. What is likely to be the "worst" fuel supplied?

3. What auxiliary fuel may be made available during periods of temporary suspension of coal delivery?
4. What type of equipment is best suited to the experience of the operating personnel?
5. In the public interest, for better public relations, or to comply with civil regulations, what is required to limit atmospheric pollution from dust?
6. What method of final refuse disposal is available?

Answers to these questions make it possible to select proper equipment for the specific method of utilizing the coal. For instance, coal should not be burned in a slag-tap furnace if the ash fusion temperature and viscosity are higher than experience indicates they should be for successful tapping. Slag-tap furnaces are rarely suitable for an ash viscosity greater than 250 poise at 2600F. If the ash viscosity of the coal selected is too high or marginal, equipment permitting the ash to be removed in dry form is indicated.

#### Ash erosion

Ash erosion must not be ignored even though coal-ash particles may be exceedingly fine. Where ash particles are concentrated in a local region, such as in a gas turn, erosion is a potential problem. The induced draft fan is a well-known example, and erosion is an important fac-

tor to be considered in selecting the type of fan and its performance characteristics. Blade wear is relatively low at fan-blade-tip speeds under 22,000 ft/min. Above this tip speed the wear from erosion increases very rapidly and higher speeds should not be considered in designs having a high concentration of entrained ash. Local high concentrations of ash through the boiler setting may cause erosion of highly critical pressure parts. This action is liable to be found where ash tends to concentrate in streams, as at turns formed by baffles within boiler banks. In this case the remedy is to limit gas velocities and to eliminate baffles if possible. The elimination of baffles has been the trend in the development of coal-fired boiler units, as illustrated in Fig. 11, where the gas flow continues horizontally through the tube banks without turns. Maximum allowable gas velocities with various fuels are given in Table 4.

**Table 4**  
Design gas velocity, fps, through net free flow area  
in tube banks to prevent flue-dust erosion

Type of Firing or Fuel	Baffle Arrangement	
	Multi-pass	Single pass
Pulverized coal	75	75*
Spreader stoker	50	60
Chain-grate stoker, anthracite	60	75
Chain-grate stoker, coke breeze	60	75
Chain-grate stoker, bituminous	100	100
Underfeed stoker	75	100
Blast-furnace gas	75	100
Cyclone Furnace	—	100
Wood or other waste fuels containing:		
Sand	50	60
Cement dust	—	45
Bagasse	60	75

\*For PC units burning fuels having more than 30% ash on a dry basis, limit the maximum velocity through the free flow area to 65 fps. For PC units burning coals producing fly ash with known high abrasive tendencies, such as Korean or Central Indian coals, limit the maximum velocity through free flow area to 45 fps.

Erosion may also be a problem in slag- and ash-handling equipment. If the unit is of the slag-tap variety, the molten refuse or slag tapped from the furnace must be cooled to be conveniently handled. This is done with water and the quenched product is usually small particles, like coarse sand, which, regardless of the mode of transport, tend to wear the surfaces of the conveying system. When water is used for transport, the pump, pipe lining, and turns in pipes or sluices are especially subject to localized wear and are usually protected by replaceable linings of alloy steel or chilled cast iron.

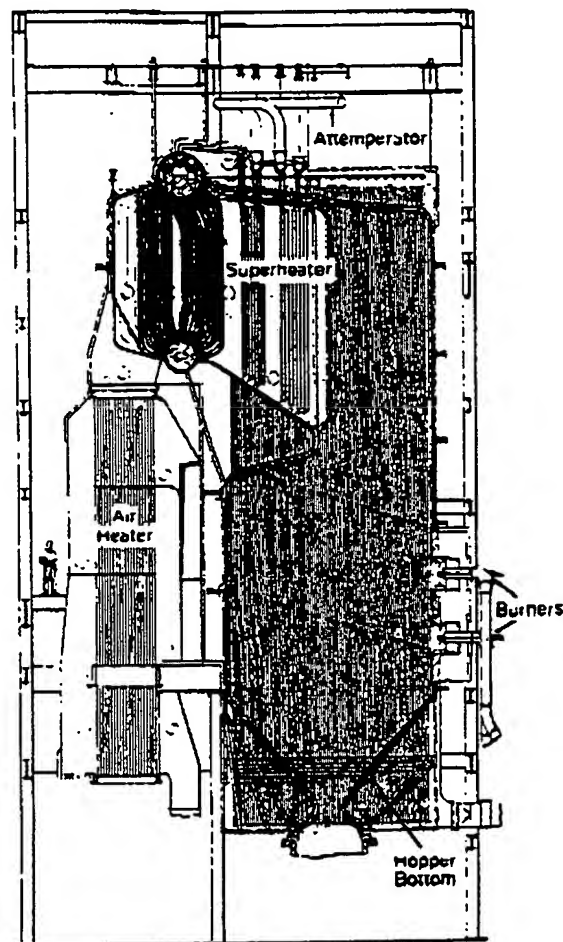
### Design and operation of slag-tap units

The method of disposal of coal ash by tapping from a boiler furnace was evolved in 1926, more by accident than by design, in a boiler furnace originally expected to operate under dry-ash disposal conditions. During operation, the low-fusion ash melted, collected in a pool at the bottom of the furnace, and was drained at intervals by means of an improvised arrangement.

Many features of this furnace, the forerunner of later slag-tap furnaces, were totally inadequate for the for-

mation, retention and disposal of fluid ash. The furnace bottom was of ordinary brick that quickly disintegrated under the chemical action of the molten slag. It was also apparent that the proper handling of a stream of molten slag was a difficult undertaking. Nevertheless, this early experience opened the way to the development of a method for easier handling and disposal of refuse in furnace operations. Some of the important requirements for adequate slag-tap furnace design that evolved from this development are:

1. The slag in the furnace must be kept fluid. The furnace temperature must be high and the slag-tap furnace should be designed to withstand the maximum temperature reached during combustion, which is usually in excess of 3000F.
2. Since fluid slag is heavy as well as extremely hot, it must be securely contained in those regions of the furnace where it tends to collect.
3. The interior surface of the furnace must be chemically inactive to the constituents of the hot slag.
4. Means must be provided to drain slag from the furnace as fast as it is formed, or at least at frequent intervals.
5. Once the molten slag has left the furnace, it must be cooled to a temperature that renders it suitable for ultimate disposal.



**Fig. 11** Boiler with dry-ash furnace designed for horizontal gas flow through tube banks without baffles.



To withstand the high temperatures noted above, all sides and the floor of the furnace are water cooled. More or less unsuccessful attempts were made at different times to employ other arrangements, including solid refractories in brick and molded form, air-cooled refractories, and water-cooled tubes on various centers embedded in a variety of refractories.

The continuous-tap arrangement for withdrawing molten slag from the furnace is illustrated in Fig. 12. The molten slag disintegrates as it comes in contact with water in the slag tank, and this final slag product is conveyed to disposal.

The difficulty in tapping slag of high fluid temperature is most evident during low-load operation. Under these conditions, even a coal with a slag of medium fluid temperature may not be suitable for slag-tapping, since the furnace temperature may not be sufficiently high to attain the degree of fluidity necessary for tapping.

One of the most important attributes of the slag-tap furnace is the coating of sticky ash that covers a portion of the furnace walls near the bottom. The sticky surface of molten ash, deliberately maintained in selected high temperature zones, serves to entrain other transient particles. The ash so collected drains continuously toward the furnace bottom and is removed through the tap holes. The consequent reduction in the quantity of dust and ash leaving the boiler unit has a definite practical value, since it decreases the amount of dust to be handled by collectors and therefore decreases the size and cost of the dust collecting equipment.

It may be possible to reduce building costs in housing units with slag-tap furnaces, since they are usually built with flat floors, thus requiring less building height. In planning new buildings, this may be a significant factor in total first cost. Even in outdoor installations the height of the supporting steel structure can be reduced. Also, slag-tap units may be installed in older plants where it would be difficult, because of the greater height required, to install a unit designed for dry ash removal.

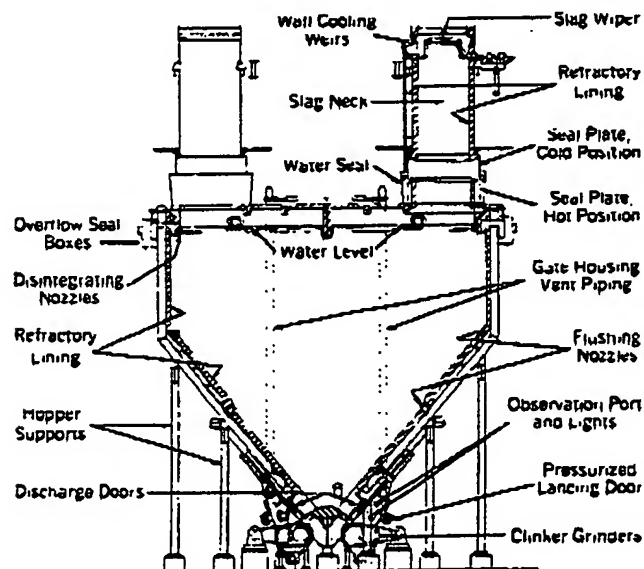


Fig. 12 Slag tank for a large utility unit for collecting low-viscosity molten ash when burning a midwestern coal. (Courtesy Allen-Sherman-Hoff Company.)

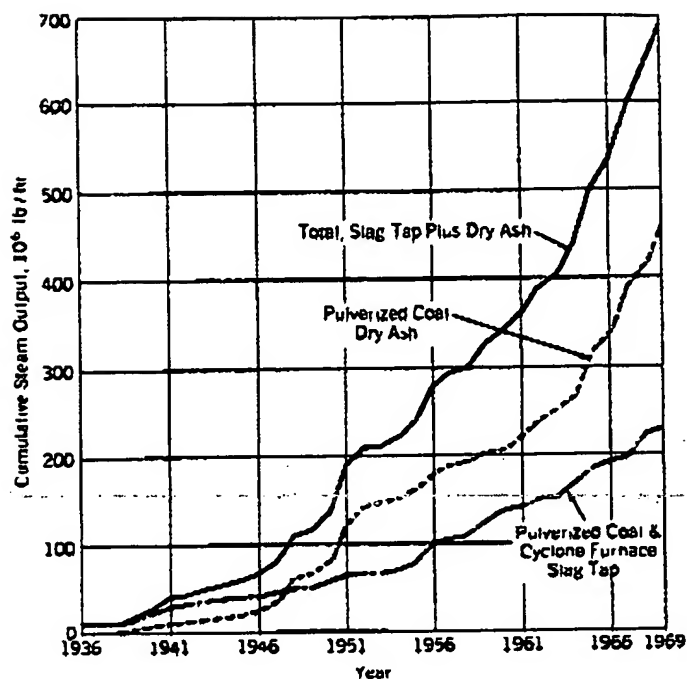


Fig. 13 Steam capacity of B&W slag-tap and dry-ash boiler units of 300,000 lb/hr and above, for a 34-yr period.

### Dry-ash and slag-tap furnace installations

For the 34-year period 1936 through 1969, B&W sold 567 slag-tap and dry-ash boiler units in sizes of 300,000 lb of steam per hr and above, for a total capacity of over 683,000,000 lb of steam per hr. Of these, 208 units for 228,000,000 lb/hr, or 33% of the total, were of the slag-tap type, and 359 units for 455,000,000 lb of steam per hr were of the dry-ash type. In the size range considered, the steam output of B&W dry-ash and slag-tap units by years is shown graphically in Fig. 13. In the earlier years of the period, the greater part of the steam output was produced with slag-tap units. In the middle years of the period, the proportion of dry-ash units steadily increased, and in 1948 virtually an equal amount of steam was produced by each type. In the years 1948 through 1969 more steam was produced by dry-ash units than by the slag-tap type.

The statistics plotted in Fig. 13 for the units included in the study, indicate a steep increase in the application of the dry-ash method of burning pulverized coal after the early period. One important reason for this increase is the fact that boiler designers, by improvements in burners, furnace proportions, and the arrangement of heating surfaces to preclude slagging and fouling, largely overcame the earlier difficulty of keeping the dry-ash unit free of slag or troublesome ash.

### Ash and slag removal from heating surfaces

Furnace walls and convection-pass surfaces can be cleaned of ash and slag while in operation by the use of sootblowers using steam or air as a blowing medium. Tubular air heaters having tubes 20 feet long or less can be cleaned by air or steam blowers. With tubes over 20 feet long, cleaning is done by circulating metal shot through the tubes for ash removal.

## Coal-ash deposition

Ash deposition in various boiler zones is an important factor to be considered by the boiler designer and operator. Initially, ash deposits on furnace walls act as insulation, thereby delaying cooling of flue gases. This can cause an increase in steam temperature and is one factor that can cause the deposits to advance into normally cooler parts of the boiler. If the deposits are not removed during operation, accumulations forming on furnace walls may cause excessive gas temperatures downstream, or in some cases, these accumulations may fall and damage pressure components. Accumulations in tube banks may block gas passes and require a boiler outage for manual cleaning.

The occurrence and severity of ash deposition depend largely on the coal-ash composition and amount of coal ash, but can be strongly influenced by the method of firing, design of equipment, and the operating conditions. Some of the influencing conditions are shown in Table 5. In practice, the design parameters and operating conditions are determined by the characteristics of the ash. For example, if the ash does not tend to form troublesome deposits, the furnace wall surfaces will require few, if any, sootblowers for cleaning. The boiler can be designed with deep banks of closely spaced superheater or reheater tubes located in high-gas-temperature zones. Relatively few sootblowers will be required and these can be operated at high speeds, with small nozzles and low pressures.

On the other hand, if the ash produces hard, massive deposits, the superheater and reheater tube banks are designed to permit ease of deposit removal. For instance, lateral tube spacing is increased, tube bank depth is decreased, and the banks are located in cooler-gas-temperature zones. Additional sootblowers, operating at maximum capability, may be required.

It is therefore essential to identify the factors responsible for the fouling characteristics of various coals, so that the optimum design can be achieved with the coal or coals being burned. This has required a large amount of research into the nature of coal and coal ash, the extent and nature of ash deposits, the relationship between coal-ash composition and ash deposition, and the effect of boiler operating variables. The results of some of this research were discussed earlier in the chapter when it was noted that coal ash was derived from mineral matter associated with the coal-forming plants and from inorganic constituents added to the coal deposit from outside sources during or following coal formation. These materials are usually referred to as inherent and adventitious mineral matter, respectively. They occur in many forms, including shales, kaolins, sulfides, carbonates, chlorides and others. Identification of the mineral species is difficult for a variety of reasons. However, the presence of several of them has long been associated with severe ash deposition, fouling, and corrosion, after the organic material is burned and the inorganic constituents are carried through the boiler by the flue gases.

An obvious answer to the problem is to remove all of the coal ash. Although some ash removal is possible and actually accomplished commercially, the task is very

difficult, and economic and technical limits are encountered. Therefore, it is imperative to acquire a comprehensive understanding of the nature of coal ash and its behavior during and following the combustion process. This is being accomplished through laboratory, pilot-plant, and field investigations being carried out in the U.S. and abroad.

The results of some of these investigations are given in the following section which briefly reviews some of the ash-deposit types and their effect on boiler operation, outlines some of the factors affecting ash deposition, and describes techniques used to assess deposit severity.

### Ash-deposit types

A portion of the coal ash and its combustion products is carried by the flue gases through the boiler, regardless of the method of coal firing. Much of the ash passes through the boiler without depositing or, in the case of the slag-tap furnace, is removed as molten slag. The ash passing through the boiler is subject to various chemical reactions and physical forces which lead to deposition on stationary surfaces. Flue-gas, particle and surface temperatures, gas velocity, flow patterns, as well as other factors such as particle size and composition, influence the amount and nature of ash depositing on cooled surfaces. Deposits are frequently divided into three broad types:

1. Fused slag deposits forming on furnace walls and other surfaces exposed to predominantly radiant heat transfer.
2. High-temperature bonded deposits occurring on convection heating surfaces, especially superheaters and reheaters.
3. Low-temperature deposits occurring on air heaters and economizers.

### Fused slag deposits

Slag deposits are usually associated with physical transport of molten or tacky particles by the flue gases. Condensation of species vaporized by the flame also can occur as the gases cool, causing enrichment of certain elements in the wall-slag deposits. For slag-tap furnaces, a portion of the furnace is usually designed to provide a continuous layer of slag near or in the combustion zone. Beyond the slagging zone, and in dry-ash pulverized coal boilers, accumulation of deposits can cause the problems described earlier. Fig. 14 shows an example of severe slagging encountered on one boiler. Deposits forming beyond the slagging zone are normally removed with short retractable sootblowers. Removal of some slags can be very difficult, depending on several factors that are discussed later.

### High-temperature bonded deposits

The formation of deposits on convection heating surfaces has been the subject of a great deal of research. The extent of these deposits varies greatly from coal to coal and with changes in the furnace wall condition. They can be very troublesome because they can obstruct gas passages, and are sometimes very difficult to remove with normal in-service cleaning equipment.

Investigators have identified several types of bonded deposits, including alkali, calcium, phosphorus, and silica

**Table 5**  
**Design parameters—coal and coal ash**

<b>Fuel characteristics</b>									
<b>1. Properties of coal substance</b> <ul style="list-style-type: none"> <li>a. Physical, including density, hardness, specific heat, thermal expansion and thermal conductivity.</li> <li>b. Chemical—behavior during heating, i.e., carbonization, gasification, and combustion.</li> </ul>	<b>2. Properties of coal ash</b> <p>Determined by the concentration and type of minerals in the coal containing the following elements.</p> <table border="0"> <tr> <td>a. Alkalis</td><td>e. Calcium-Magnesium</td></tr> <tr> <td>b. Sulfur</td><td>f. Iron</td></tr> <tr> <td>c. Chlorine</td><td>g. Silica</td></tr> <tr> <td>d. Phosphorus</td><td>h. Alumina</td></tr> </table>	a. Alkalis	e. Calcium-Magnesium	b. Sulfur	f. Iron	c. Chlorine	g. Silica	d. Phosphorus	h. Alumina
a. Alkalis	e. Calcium-Magnesium								
b. Sulfur	f. Iron								
c. Chlorine	g. Silica								
d. Phosphorus	h. Alumina								
<b>Technological properties</b> <ul style="list-style-type: none"> <li>1. Proximate analysis</li> <li>2. Ultimate analysis</li> <li>3. Free-swelling index</li> <li>4. Differential thermal analysis</li> <li>5. Thermogravimetric analysis</li> <li>6. Effluent gas analysis</li> <li>7. Grindability</li> <li>8. Calorific value</li> <li>9. Sieve analysis</li> <li>10. Ignitability</li> <li>11. Abrasiveness</li> </ul>	<b>Technological properties</b> <ul style="list-style-type: none"> <li>1. Fusion temperatures</li> <li>2. Viscosity of slag</li> <li>3. Surface tension of slag</li> <li>4. Volatility of constituents in slag</li> <li>5. Sintering temperature and strength of ash</li> </ul>								

### Boiler design and operation

- |  |   |
|--|---|
| <b>1. Firing method</b> <ul style="list-style-type: none"> <li>a. Slag tap, PC and cyclone</li> <li>b. Dry ash, PC</li> <li>c. Fuel bed, chain-grate, and spreader stoker</li> </ul>   | <b>4. Combustion conditions</b> <ul style="list-style-type: none"> <li>a. Excess air</li> <li>b. Air temperature</li> <li>c. Load cycles</li> <li>d. Residence time</li> </ul>      |
| <b>2. Furnace design</b> <ul style="list-style-type: none"> <li>a. Rating</li> <li>b. Wall construction</li> <li>c. Type, number and arrangement of burners</li> <li>d. Furnace geometry</li> <li>e. Exit-gas temperature</li> </ul> | <b>5. Properties of flue gases</b> <ul style="list-style-type: none"> <li>a. Temperature</li> <li>b. Flow patterns</li> <li>c. Composition</li> </ul>                               |
| <b>3. Tube bank design</b> <ul style="list-style-type: none"> <li>a. Horizontal or vertical tubes</li> <li>b. Spacing, side and back</li> <li>c. Depth of bank</li> <li>d. Alignment</li> <li>e. Freedom of tube movement</li> </ul> | <b>6. Properties of entrained ash</b> <ul style="list-style-type: none"> <li>a. Dust loading</li> <li>b. Size consist</li> <li>c. Composition</li> <li>d. Microstructure</li> </ul> |

### Sootblower design and operation

- 1. Blowing medium**
  - a. Air or steam
  - b. Pressure
  - c. Temperature
- 2. Type of sootblower**
  - a. Short retractable
  - b. Long retractable
  - c. Fixed position rotating
  - d. Traveling frame
- 3. Location and spacing of sootblowers**
- 4. Sootblower nozzles**
  - a. Type
  - b. Size
  - c. Number
  - d. Angle of attack
- 5. Lance-tube speed**
  - a. Rotational
  - b. Axial
- 6. Frequency of blower operation**

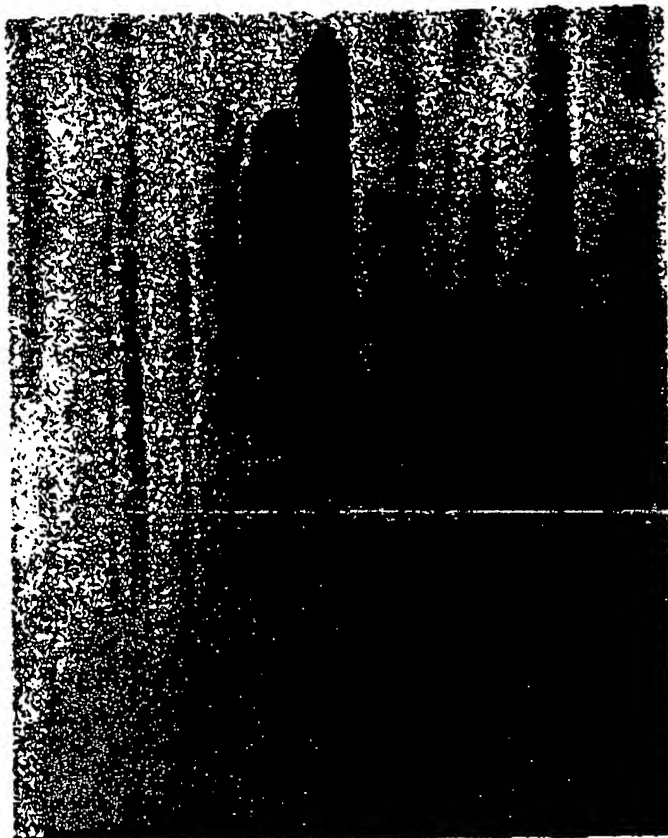


Fig. 14 Furnace-wall slag deposits.

types, depending on the bonding agent. They appear to be associated with vaporization of coal ash constituents during combustion and subsequent condensation on fly-ash particles on surfaces. The alkali and calcium-bonded deposits are more common in the United States, whereas problems with these and the other types have been described by investigators in other countries. The occurrence and severity of fouling by these bonded deposits depend chiefly on the composition of the coal ash, but are influenced by the method of firing, the design of equipment, and the conditions of operation.

Since the alkali-bonded deposits are generally acknowledged as the most prevalent, especially with U.S. bituminous coals, they will be treated more extensively in the following sections. An example of severe fouling on superheater tubes is shown in Fig. 15.

Deposits found in the superheater and reheater regions of the boiler are typically composed of a thin inner layer with a characteristic composition and appearance distinctive from the outer layer, which has a composition similar to the fly ash. Table 6 gives a comparison of the two deposit layers and the fly ash from a boiler firing an Illinois coal.

The inner layer is normally tightly attached to the tube surface and there is strong evidence that a liquid phase exists within the layer at operating temperatures. This layer provides a bond between the superheater tube and the outer layer of sintered fly ash which forms the bulk of the deposit and becomes massive under certain conditions.

It is apparent that the inner layer is rich in sodium and potassium, and it usually contains sulfate in excess of

Table 6  
Analysis of superheater deposits vs fly ash  
from a boiler firing an Illinois coal

Constituents of Ash, % by Wt	Fly Ash	Superheater Deposits	
		Outer Layer	Inner Layer
SiO <sub>2</sub>	37.4	36.2	15.8
Al <sub>2</sub> O <sub>3</sub>	15.3	12.9	9.0
Fe <sub>2</sub> O <sub>3</sub>	20.8	19.9	11.8
TiO <sub>2</sub>	1.0	1.1	0.5
CaO	5.2	9.1	3.9
MgO	0.9	1.0	0.8
Na <sub>2</sub> O	3.8	4.3	5.9
K <sub>2</sub> O	2.7	2.4	9.0
SO <sub>3</sub>	8.6	13.1	43.3
Not Determined	3.3	0.0	0.0
Total	100.0	100.0	100.0
Water Solubility, %	—	12	60

the normal alkali equivalent, which is attributed to the formation of complex iron and aluminum sulfates. Investigations carried out by B&W indicate that this white inner layer is formed over a period of time as a reaction product of the gaseous sulfur oxides and fly ash depositing on tube surfaces. Inspections and analyses were made of deposits forming on an air-cooled probe in a boiler firing an Illinois coal. After one week of exposure to flue gases at approximately 2000F, the deposit formed on the metal surface, controlled at 1050F, consisted of loosely held fly ash with no evidence of a white bonding material. The white layer began forming after two weeks and its thickness progressively increased throughout the remainder of the 11-week test period.

The white layer not only provides a bond for the bulk fly-ash deposit, but can also be responsible for corrosion of high temperature tubes. This is discussed in a subsequent section in this chapter.

The nature and amount of bulk deposit forming on the tube are functions of fly-ash characteristics, which in turn are related to the coal-ash composition, firing method, and furnace operating conditions. For fly ash with similar properties, the rate of ash deposition is proportional to the amount of fly ash being transported by the flue gases.

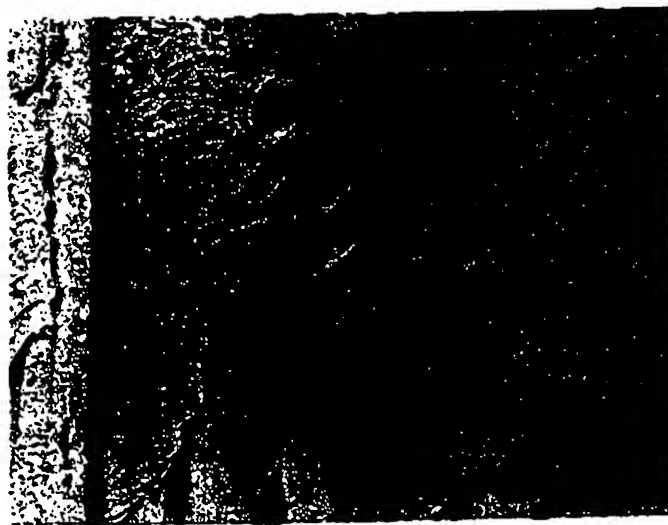


Fig. 15 Ash deposits on secondary superheater tubes.

### Low-temperature deposits

Formation of deposits in the low-temperature zones such as the economizer and air heater is usually associated with condensation of acid or water vapor on cooled surfaces. Other types of deposits, especially in the economizer of boilers with bed-type combustion systems, have also been reported while firing coals with relatively small amounts of phosphorus. Phosphatic deposits have been extremely hard, but the problem is restricted to a limited number of boilers, located mostly in Europe.

Condensation of acid or water vapor can be encountered when metal surfaces are allowed to cool below the acid or water dew points. The sulfuric acid dew point depends on the amount of sulfur trioxide present in the flue gases, but it is usually between 250 and 300F for  $\text{SO}_3$  concentrations of 15-30 parts per million. The water dew point depends on the coal and air moisture levels, the hydrogen in the coal, the excess air, and the amount of steam used in sootblowing. It is usually in the range of 105-115F for coal firing. On air heaters, where metal temperature is a function of both air and flue gas temperatures, condensation on low temperature surfaces of tubular heaters can occur on tubes near the air inlet and flue gas outlet or on cold-end baskets on regenerative heaters as they are being heated by the flue gases on each cycle. Several factors, such as maldistribution of air or flue gases, excessively low exit-gas temperatures and very low air temperatures can aggravate the problem of condensation. Low gas flow during low load, start-up and other similar periods can also result in condensation of water and acid.

The deposits themselves can be composed of three types of material. First, the acid attack can produce various amounts of corrosion product next to the metal depending on the amount of acid available, the temperature, and the type of metal. Second, this wet deposit can trap fly ash which adds to the bulk of the deposit. Third, the acid can react with constituents such as iron, sodium and calcium in the fly ash to form sulfates, which increase the deposit bulk.

The deposits are usually characterized by low pH (highly acidic); many contain hydrated salts, and for most bituminous coals they are water soluble. In this case, deposits can sometimes be water washed from low-temperature surfaces. However, in some cases when the coal ash contains large amounts of materials such as calcium, the reaction product  $\text{CaSO}_4$  is nearly insoluble. The deposits that form are very hard and difficult to remove by washing. Complete plugging of gas passes also makes removal by water washing more difficult, even when the deposits are water soluble.

Deposition can be eliminated by operating the metal temperatures well above the acid dew point temperature of the flue gas, but this would result in a significant loss in boiler efficiency. Improvements in design to get more uniform air and gas distribution, better materials of construction and improved cleaning systems have been combined to minimize the low-temperature deposit problem while operating at relatively low exit-gas temperatures.

### Evaluation techniques

The development of laboratory techniques for evaluating the slagging and fouling tendencies of coals is an important and necessary step in providing optimum boiler designs for each fuel type. Typical ASTM tests are usually inadequate to distinguish fouling tendencies of various coals. Extremes in ash fusion temperatures may be indicative of differences in fouling and slagging potential, but most coal ash falls within a narrower range and the fusion temperatures are therefore inadequate. Operating experience from commercial boilers is essential in establishing the actual behavior of coals, but controlled testing of large boilers is unwieldy and expensive. Furthermore, it is impossible in these large boilers to examine very small coal samples, such as core drillings from a new mine. Thus, information that would be of value in establishing boiler and cleaning equipment design parameters might be delayed, probably until a new mine is operating, and the boiler has already been designed. It is therefore essential that laboratory tests be available to evaluate the behavior of coals. Several methods have been developed by B&W to aid in providing optimum design parameters for various coal-ash types.

#### Wall slagging

The deposit forming on water-cooled furnace walls usually varies in appearance, depending on the composition, atmosphere, and slag temperature. Adjacent to the tube surface, it is frequently porous and relatively loosely adherent to the tube surface. As the deposit builds in thickness, the surface exposed to the flue gases becomes plastic, then fluid, if temperatures are high enough when it reaches an equilibrium thickness. However, the plastic slag is more difficult to remove as sootblowers can be almost ineffective in penetrating the viscous plastic shell that sometimes forms at the outside surface of the wall slag.

Various methods have been used in attempting to predict the slagging tendencies of a coal ash. Ash fusion temperatures, in some cases, provide an indication of the potential problems that might be encountered with a particular coal. For example, coal ash with extremely high fusion temperatures remains dry and little or no deposit forms on furnace walls. However, for coals with lower ash fusion temperatures, other factors are important. Coal-ash composition has also been shown to influence the slagging behavior of coal ash and formulas have been proposed to calculate softening temperature from ash composition, but here too, no correlation has been developed to enable prediction of wall-slagging tendency.

Extensive field tests, during which time-lapse movies and other observations were made, confirmed that the slags that were plastic were very difficult to remove. Viscosity measurements, usually made to determine flow characteristics for slag-tap performance, were extended to higher viscosity levels. These measurements showed that the slags most difficult to remove were plastic over a broad temperature range, whereas slags that were easy to remove were plastic over a relatively narrow temperature range (see Fig. 16). This relationship was observed for a number of coal-ash slags and efforts are

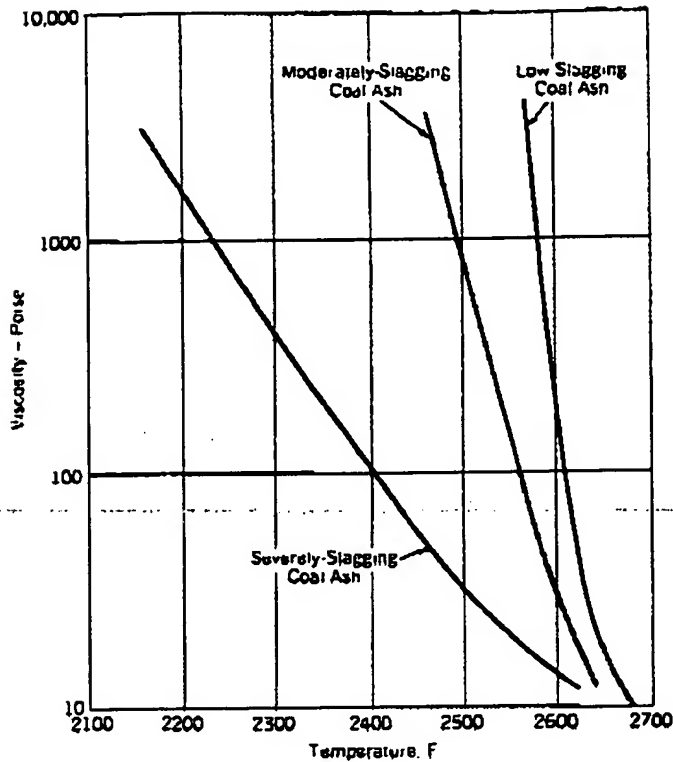


Fig. 16 Viscosity of wall slags (oxidizing atmosphere).

now being made to develop a correlation giving coal-ash viscosity in the plastic region as a function of temperature and slag composition, including relative amounts of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ . The influence of the iron oxidation state is very strong and the change in oxidation level may be due to changes in excess air. Fig. 17 shows the effect on viscosity by changing from an oxidizing to a reducing atmosphere over the slag melt. Flame impingement on furnace water walls can be responsible for creating a strongly reducing condition of the slag and causing severe wall slagging.

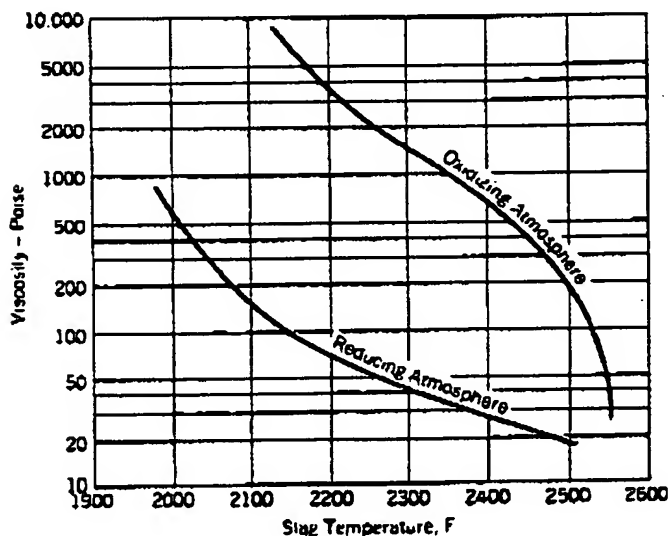


Fig. 17 Viscosity-temperature relationship.

### High-temperature bonded deposits

Early research effort in this area was directed toward alleviating ash deposition by modifying boiler design, injecting additives, and improving boiler cleaning equipment. During this time, numerous coal analyses were obtained in an effort to isolate troublesome coal constituents, and concurrently to develop laboratory techniques for assessing the deposit-forming tendency of a coal. One technique, developed some time ago, has proved to be very useful and is still in use today. This technique, called the sintering test, determines the relative strength of a deposit. In this test, the fly-ash samples collected from the flue gases are passed through a 60-mesh U.S. Standard screen to remove particles of slag and are then ignited to constant weight at 900F to remove any carbon that might be present. The ignited fly ash is then reduced to a minus 100-mesh size, and at least 24 cylindrical specimens (0.6-in. diameter by 0.75-in. long) are formed in a hand press at a pressure of 150 psi. At least six specimens are heated in air, usually at each of four temperature levels (1500, 1600, 1700 and 1800F) for 15 hours.

After the specimens have cooled slowly in the furnace, they are removed, measured, and then crushed in a standard metallurgical testing machine. The sintered or compression strength is then computed from the applied force and the cross-sectional area of the sintered specimen. The average strength of six specimens is used as the strength of the sintered fly ash at a particular sintering temperature.

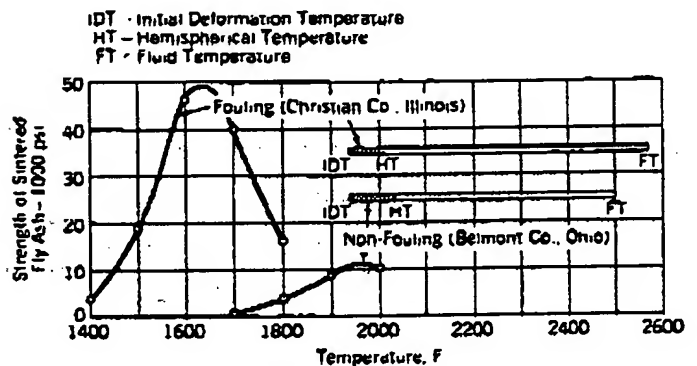


Fig. 18 A comparison of sintered strengths and ash fusion temperatures for a fouling and a non-fouling coal.

Extensive application of this method, combined with observation of operating boilers, showed that coals with a tendency to form troublesome deposits produced fly ash with high sintered strength. Conversely, low-strength fly ash was associated with non-fouling coals. The two extremes are illustrated in Fig. 18 which shows the strength of sintered fly ash for two coals having similar ash fusibility but widely varying fouling characteristics. This figure shows that ash fusion temperatures bear little relation to the tendency to form bonded deposits.

Coal samples were also obtained while the sintering information was being compiled. A relationship between total alkali content ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , expressed as equivalent total  $\text{Na}_2\text{O}$ ) and fly-ash sintered strength was observed for the samples collected. This trend is shown in



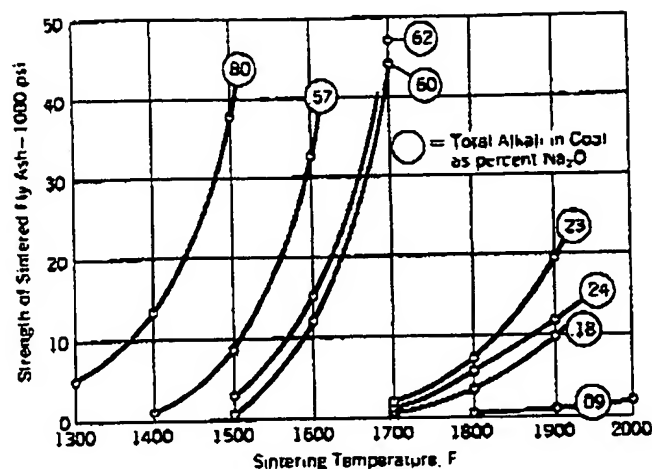


Fig. 19 Effect of alkali content in coal.

Fig. 19, which illustrates the higher coal-alkali content associated with high-strength fly ash. As knowledge of the factors affecting ash deposition increased, guidelines were established to arrive at suitable equipment designs for various fuels. The first such guideline, called a "fouling index," used total alkali content in the coal as a criterion. This index divided coal into three categories, based on the alkali content. Coals with 0.4% alkali or lower produced deposits that could easily be removed by sootblowers, but superheater fouling increased markedly when the alkali content of the dry coal was more than 0.6%. Between these two levels, intermediate fouling was encountered.

During this period, it was also learned that additives such as dolomite and magnesite have a pronounced effect on the strength of fly ash. For bituminous coals, which normally contain more acidic than basic constituents, magnesite was the most effective additive tested. Fig. 20 shows the effect of several additives. Subsequent field tests in which magnesite and high-magnesite dolomite were injected into boilers, confirmed that these additives could substantially lower sintered strength and reduce fouling with bituminous coals.

#### Development of laboratory tests

The fouling guidelines were improved as information was acquired from operating experience, sintering data, and coal analyses. However, the acquisition of data for improving guidelines was slow and expensive because it was dependent on field tests. This, of course, meant full-scale boiler tests under constant conditions with a large, consistent coal supply which became more difficult as unit size increased. In an effort to improve the efficiency and accuracy of obtaining data, a research program was initiated to develop a technique to evaluate the fouling potential of a coal based on information developed in the laboratory. The primary requirement for this step was the production of suitable fly ash for evaluation by the sintering test. This was accomplished by building a small coal-fired pilot plant.

Tests made in the pilot plant confirmed field experience, indicating that it could be used as a tool for evaluating ash-fouling tendency. Fig. 21 shows that fly ash from this pilot plant had widely differing strengths; those strengths related well with fouling history.

Numerous tests have been made with a variety of domestic and foreign coals. These coals were selected to provide a wide range of analyses and fouling potential when this information was known. The actual ranges of concentrations of coal-ash constituents for all coals and for the bituminous coals tested in this and other programs are compared in Table 7 with the ranges typical of U.S. coals:

Table 7  
Coal-ash constituents of pilot plant coals vs typical U.S. coals  
Percent by weight

	All Coals Tested	Bituminous Coals Tested	Typical U.S. Coals
SiO <sub>2</sub>	3.3-61	37-61	20-60
Al <sub>2</sub> O <sub>3</sub>	<50-43	13-43	10-35
Fe <sub>2</sub> O <sub>3</sub>	2.6-30	2.6-30	5-35
TiO <sub>2</sub>	0.3-1.4	0.7-1.4	0.5-2.5
CaO	0.9-33	0.9-9.2	1-20
MgO	0.4-10+	0.4-2.4	0.3-4
Na <sub>2</sub> O	0.1-14	0.1-2.4	1-4
K <sub>2</sub> O	0.2-3.0	0.3-3.5	
SO <sub>3</sub>	1-23	-	0.1-12

This comparison shows that information has been acquired for coals with constituent concentration ranges in some cases greater than those typical of U.S. coals, and thus indicates a very wide range of coal-ash compositions.

These experiments have demonstrated that sodium is the most important single factor affecting ash fouling. Potassium, which had been included in previous alkali-fouling indices, makes no perceptible contribution to sintered strength. The amount of water-soluble sodium, which is related to the more readily vaporized sodium, was shown to have a major effect on sintered strength.

This result was achieved by washing the coal with hot condensate in the laboratory to remove the water-soluble sodium which is related to the more readily vaporized

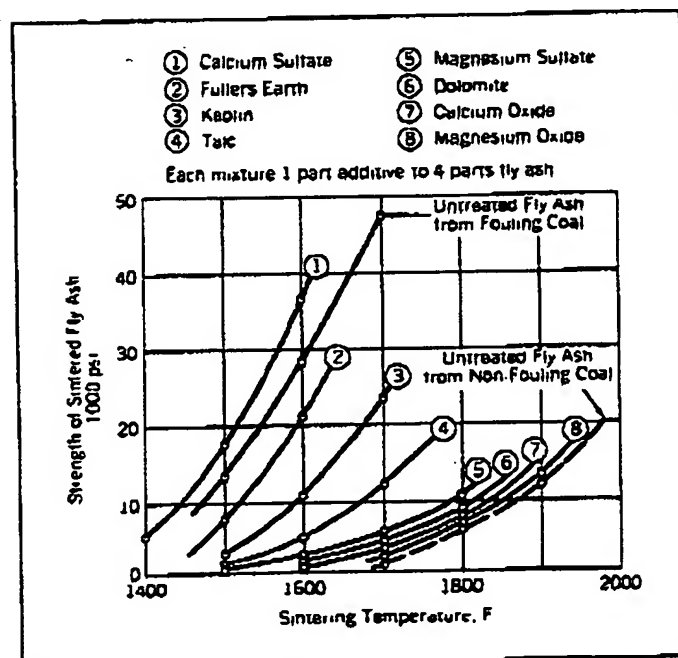


Fig. 20 Effect of additives.

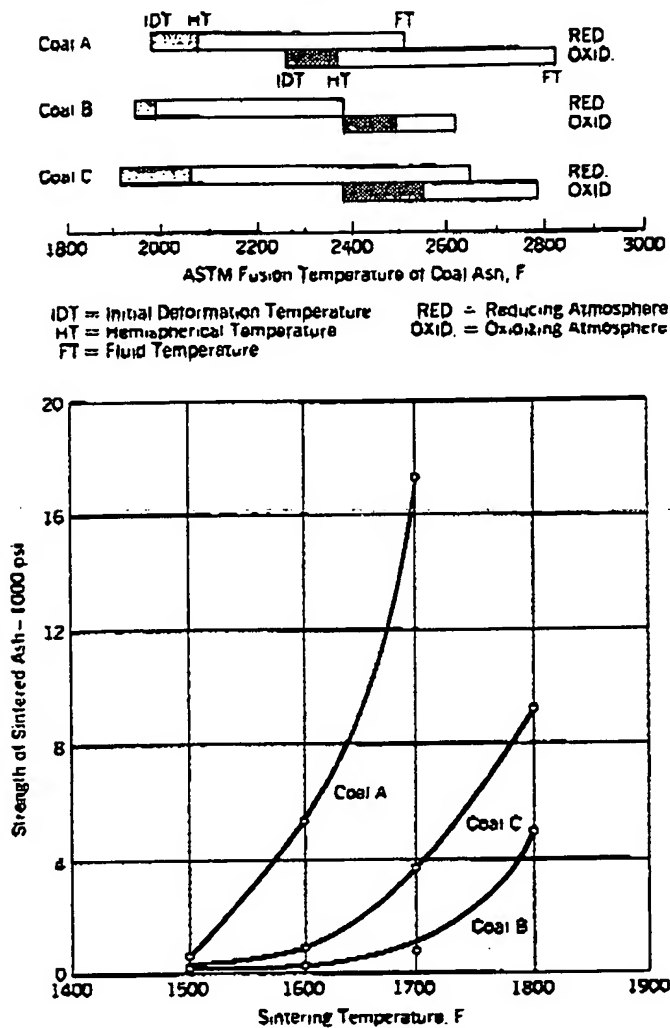


Fig. 21 Comparison of sintering characteristics of laboratory fly ash.

sodium. The washed coal was then fired in the pilot plant and sintered at various temperatures. In one case a fouling coal washed with hot condensate and sintered at 1700F had a fly-ash strength only 10% of the value obtained with an unwashed sample at the same sintering temperature.

Information from the tests carried out thus far is being processed to develop correlations between fly-ash sintered strength and coal-ash composition, using both total and water-soluble sodium.

#### Lignites

Tests with several North Dakota and Canadian lignites, and an Australian brown coal, all of which have ash with high alkali contents ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ), have shown that fly ash from these coals will sinter at low temperatures, but sintered strengths remain low regardless of fouling tendency. Since this ash contains large amounts of alkaline materials, which react with sulfur dioxide to form sulfates, the bond is probably a sulfate type.

#### Effect of operating variables

Although the predominant factors affecting ash deposition are the amount and composition of the coal ash,

boiler operating conditions have also been demonstrated to affect deposition. Some of the factors that have been studied are excess air, firing method, and deposit-time temperature, which is a function of the gas-tube temperature relationship as well as ash properties.

The effect of excess air variation on viscosity is indicated in Fig. 17. It was noted earlier that plastic slag is most difficult to remove from furnace walls, and this figure shows that variations in atmosphere from reducing to oxidizing have a major effect on the nature of the ash. In practical terms, this means that care must be exercised in maintaining proper coal/air ratios at all times. If imbalances are allowed to occur, the slagging may be aggravated. Flame impingement on furnace walls, or operating several burners with less than theoretical air required for combustion and others at high excess-air levels, are typical ways in which this can occur. Increased slagging can also raise temperatures entering the convection bank, which leads to higher gas and deposit temperatures, thereby increasing deposit strength (see Fig. 19). Thus, although excess air has no direct effect on deposit strength, the higher gas temperatures caused by increased furnace wall slagging do affect superheater deposition.

Since deposition appears to be associated with vaporization of coal ash constituents, this phenomenon has been studied extensively. Vaporization is strongly dependent on mineral-matter type and on time and combustion temperature. Combustion temperature in turn is affected by heat release rate (including firing method), excess air, combustion air temperature, and coal characteristics. The rate of deposition is proportional to the amount of ash suspended in the flue gases and actual operation can be more severe for the lower strength deposits because of the higher rate of deposition. For bituminous coals only a small amount, usually less than 5%, of the suspended ash is deposited on convection banks, but for lignites this figure may be much greater.

Sintering time or reaction time is also a very important factor in determining deposit characteristics. Fig. 22 shows that, if a deposit is not removed promptly, the strength of the deposit increases many times. Thus, es-

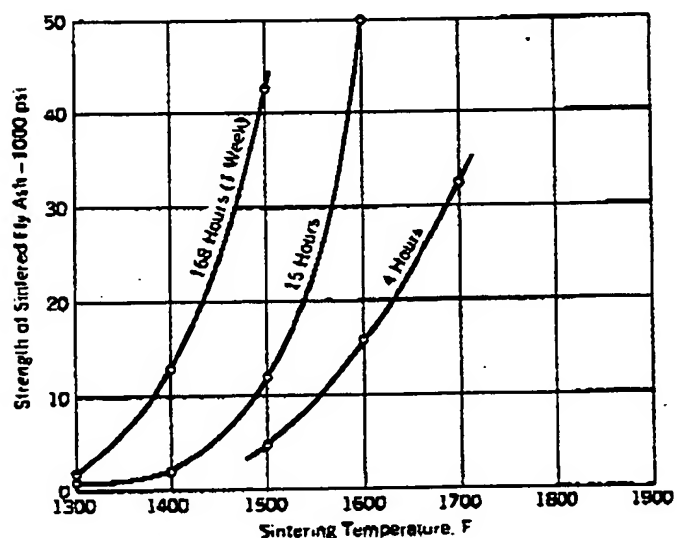


Fig. 22 Effect of sintering time.



establishing sootblower operating frequency and coverage is also an extremely important facet of the overall problem of ash deposition.

### Coal-ash corrosion

Serious external wastage or corrosion of high-temperature superheater and reheater tubes was first encountered in coal-fired boilers in 1955. Tube failures resulting from excessive thinning of the tube walls, as shown in Fig. 23, occurred almost simultaneously in the reheater of a dry-ash furnace boiler and the secondary superheater of a slag-tap furnace unit. Corrosion was confined to the outlet tube sections of the reheater and the secondary superheater, which were made from chrome-ferritic and stainless steel alloys, respectively.

Significantly, these boilers were among the first to be designed for 1050F main and reheat steam temperatures; also, both units burned high-sulfur, high-alkali coals from central and southern Illinois, which were causing chronic ash-fouling problems at the time.

Early investigations showed that corrosion was found on tube surfaces beneath bulky layers of ash and slag. When dry, the complex sulfates were relatively innocuous, but when semi-molten (1100-1350F), they corroded most of the alloy steels that might be used in superheater construction, as well as other normally corrosion-resistant materials.

At first, it appeared that coal-ash corrosion might be confined to boilers burning high-alkali coals, but complex sulfate corrosion was soon found on superheaters and reheaters of several boilers burning low-to-medium alkali coals. Where there was no corrosion, the complex sulfates were either absent or the tube-metal tempera-

tures were moderate (less than 1100F). The general conclusions drawn from this survey of corrosion were:

1. All bituminous coals contain enough sulfur and alkali metals to produce corrosive ash deposits on superheaters and reheaters, and those containing more than 3.5% sulfur and 0.25% chlorine may be particularly troublesome.
2. Deposit temperature adjacent to the tube surface is the dominant factor affecting rate of corrosion. Experience has shown that the combination of tube-metal temperature and gas temperature provides a practical criterion for estimating deposit temperature and for establishing design temperature limits. Fig. 24, which is used as a guide in design, indicates stable and corrosive zones of fuel-ash corrosion as a function of gas and metal temperatures.

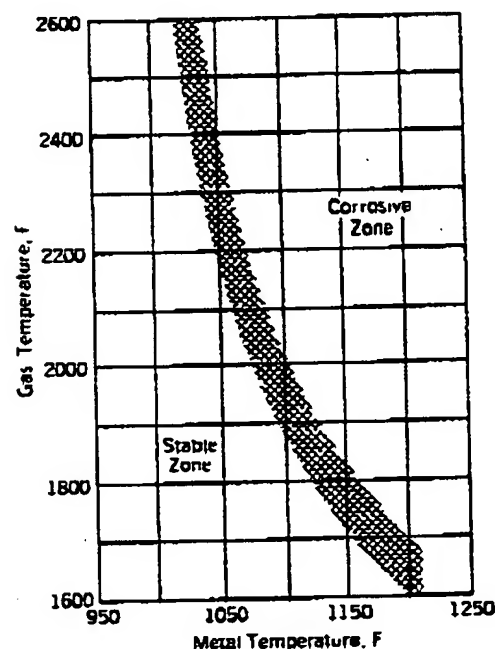


Fig. 24 Fuel-ash corrosion—stable and corrosive zones.

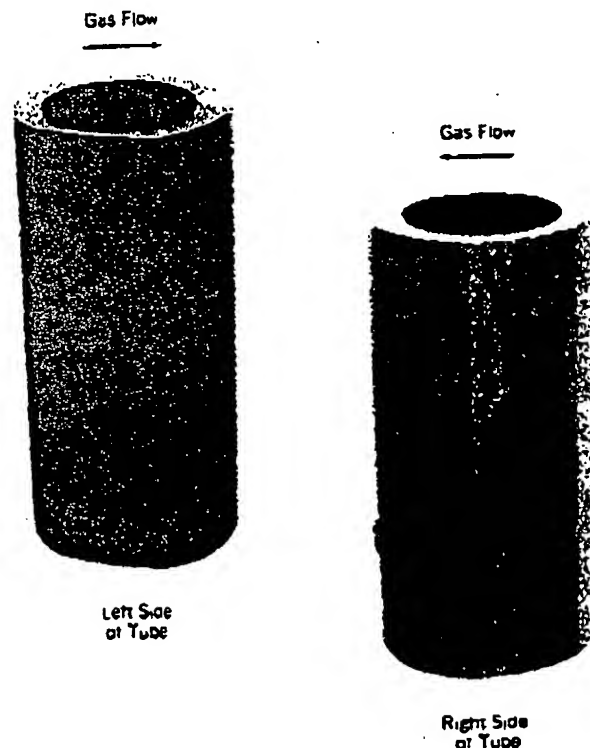


Fig. 23 Typical corroded 18Cr-8Ni tube from secondary superheater.

Based on this information, B&W modified the design of its boilers to reduce greatly the corrosion of superheaters and reheaters. These modifications included changes in furnace geometry, burner configuration, superheater arrangement, and the use of gas tempering, all of which reduced metal and gas temperatures and reduced temperature unbalances. Experience from these installations has shown that it is possible to operate boilers with main and reheat steam temperatures up to 1050F with little, if any, corrosion.

Meanwhile, there was a gradual return to the 1000F steam conditions for new plants, due primarily to economic factors and secondarily to coal-ash corrosion. This temperature level permits the use of lower-cost alloys in the boiler, steam piping, and turbine with substantial savings in investment costs, and it also provides a greater margin of safety to avoid corrosion. Steam temperatures will therefore probably remain on the current 1000F plateau until economics dictates the use of high-

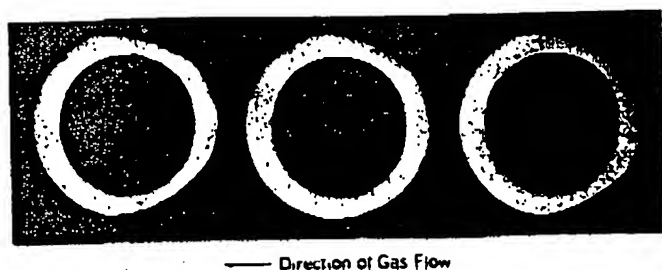


Fig. 25 Transverse sections of corroded tubes from secondary superheater platens.

temperature alloys and until methods are developed for avoiding corrosion at higher steam temperatures.

#### General characteristics of corrosion

External corrosion of superheaters and reheaters is concentrated on the upstream side of the tube, as shown in Fig. 25. The greatest metal loss usually occurs on the 10 and 2 o'clock sectors of the tubes and it tapers off to little or none on the back side of the tubes. The corroded surface of the tube is highly sculptured by a shallow macropitting type of attack. The amount of corrosion, as measured by reduction in tube wall thickness, varies considerably along the length of the tube, depending on local conditions, i.e., the position of the tube in the bank or platen, the proximity of sootblowers, the composition of ash deposits and, most importantly, the gas and metal temperatures.

The corrosion rate is a nonlinear function of metal temperature (Fig. 26). The corrosion of both chrome-ferritic and 18Cr-8Ni stainless steels increases sharply above a temperature of 1150F, passes through a broad maximum between 1250 and 1350F, and then decreases rapidly at still higher temperatures.

The highest corrosion rates are generally found on the outlet tubes of radiant superheater or reheater platens opposite retractable sootblowers. Values ranging from 50 to 250 mils/year have been observed on 18Cr-8Ni stainless steel tubes under these adverse conditions.

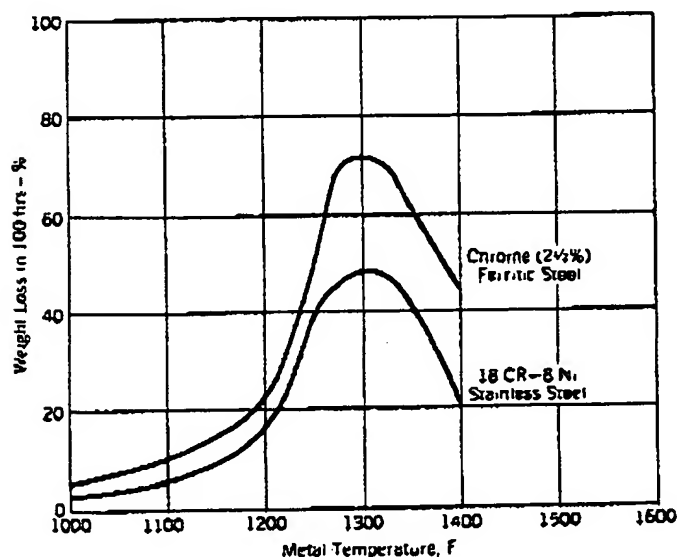


Fig. 26 Effect of temperature on corrosion rate.

When similar high-temperature surfaces (1100-1175F) are arranged in convection tube banks so they are shielded from direct furnace radiation and sootblower action, corrosion rates are much lower, ranging between 5 and 20 mils/year.

#### Corrosive ash deposits

Corrosion is rarely found on superheater or reheater tubes having only dusty deposits. It is nearly always associated with sintered or slag-type deposits that are strongly bonded to the tubes. Such deposits consist of at least three distinct layers. The outer layer, shown diagrammatically in Fig. 27, constitutes the bulk of the deposit and has an elemental composition similar to that of fly ash. Though often hard and brittle, this layer is a porous structure through which gases may diffuse. Innocuous by itself, it plays an important part in the formation of an intermediate layer that contains the corrosive agents.

The intermediate layer, frequently called the white layer, is a white-to-yellow colored material which varies in thickness from 1/32 to 1/4 in. It usually has a chalky texture where corrosion is mild or nonexistent but is fused and semi-glossy where corrosion is severe. In the latter condition this layer is difficult to remove as it is so firmly bonded to the corroded surface beneath.

Upon heating in air, the intermediate layer melts around 1000F and slowly discolors and hardens into a hard mass resembling rust. Chemical analyses of this layer show that it contains higher concentrations of potassium, sodium and sulfur than does the parent coal

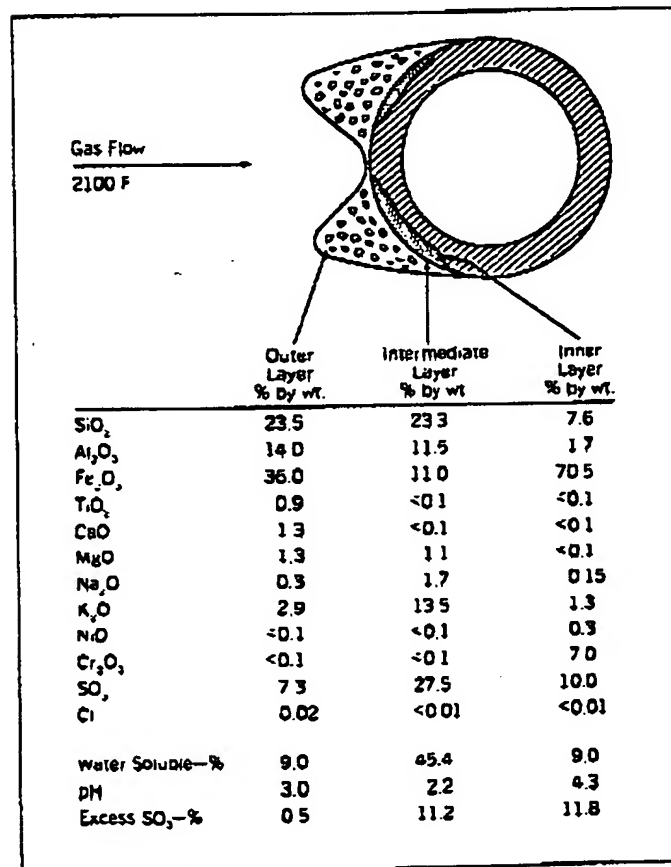


Fig. 27 Analyses of typical ash deposit from 18Cr-8Ni superheater tube.

ash. A large part of this deposit is water soluble and the water-soluble fraction is always acidic. The identification of compounds making up the intermediate layer is difficult because its constituents are not well crystallized. The normal sulfates are conspicuously absent and the complex alkali sulfates are detected irregularly. The most common compounds found are  $\text{Na}_3\text{Fe}(\text{SO}_4)_3$  and  $\text{KAl}(\text{SO}_4)_2$  although other complex sulfates are thought to be present.

Laboratory studies have shown that complex alkali sulfates, when molten, rapidly corrode most, if not all, superheater alloys. Corrosion begins between 1000 and 1150F, depending on the relative amounts of complex sodium and potassium sulfates present, and whether these are predominantly iron or aluminum-base compounds. Corrosion usually begins at the lower temperature where the sodium-iron-sulfate system is the major part of the intermediate layer, but corrosion is more severe and persists into a higher temperature range when the potassium-aluminum-sulfate system is the dominant one.

If the intermediate layer is carefully removed, a black, glassy inner layer is revealed, which appears to have replaced the normally protective oxide on the tube. This layer is composed primarily of corrosion products, i.e., oxides, sulfides and sulfates of iron, and other alloying constituents in the tube metal. It seldom exceeds  $\frac{1}{16}$  in. thickness on corroded 18Cr-8Ni stainless steel tubes, probably because of its strong tendency to spall off when the tube cools. The layer containing corrosion products from chrome-ferritic alloys often reaches  $\frac{1}{8}$  in. thickness and exhibits little tendency to spall as the tube cools.

#### Corrosion mechanisms

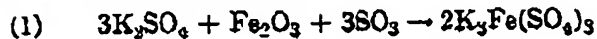
The elements involved in coal-ash corrosion (sodium, potassium, aluminum, sulfur, and iron) are derived from the mineral matter in coal. The minerals supplying these elements include shales, clays and pyrite, which are commonly found in all coals.

During the combustion of coal, these minerals are exposed to high temperatures and strongly reducing effects of carbon for very short periods of time. Although comparatively stable, the mineral matter undergoes rapid decomposition under these conditions. Some of the alkalis are released or volatilized as relatively simple compounds, which have "dew points" in the 1000-1300F range. Furthermore, the pyrite is oxidized, releasing  $\text{SO}_2$  with the formation of a small amount of  $\text{SO}_3$ , leaving a residue of iron oxide ( $\text{Fe}_2\text{O}_3$ ).

By far the largest portion of the mineral matter or its derived species react to form the glassy particulates of fly ash. The fly ash and volatile species in the flue gases tend to deposit on the tube surfaces in a selective manner and subsequent reactions between these materials occur over long periods of time.

In the formation of corrosive deposits, fly ash first deposits on the superheater and reheater tubes. Slowly, over a period of weeks, the alkalis and the sulfur oxides diffuse through the layer of fly ash toward the tube surface. In the lower temperature zone of the ash deposit, chemical reactions between the alkalis, the sulfur oxides, and the iron and aluminum components

of the fly ash result in the formation of the complex alkali sulfates as follows:



Similar reactions occur with sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), although the complex sodium sulfates are less apt to form at high temperatures because of their lower stability.

Recent work at B&W's Research Center has shown that  $\text{SO}_3$  concentrations in ash deposits must be very high (1000-1500 ppm), compared to the level in the flue gas (10-25 ppm) in order to form the complex alkali sulfates in the intermediate layer. Hence the bulk of the  $\text{SO}_3$  must come from the catalytic oxidation of  $\text{SO}_2$  in the outer layer of the deposit.

When the  $\text{SO}_3$  produced in the outer deposit exceeds the partial pressure of  $\text{SO}_3$  over the intermediate deposit, the complex sulfates form via reactions (1) and (2) above. When the opposite is true, the complex sulfates begin to decompose, according to the reverse of reactions (1) and (2), until a new equilibrium is reached. Since the formation of  $\text{SO}_3$  is temperature dependent, the reversibility of these reactions is also temperature dependent. As shown in Fig. 26, the corrosion rate increases with temperature, passes through a maximum between 1250 and 1350F, and then falls to a comparatively low level at higher temperatures.

The destructive reactions between the complex alkali sulfates and the tube metal and its oxides have not been fully defined. A number of theories have been advanced to account for the composition of the corrosion products and the high rate of metal wastage. One that has been tentatively accepted is shown below:



The temperature range of this rapid liquid-phase attack is bracketed by (a) the melting temperature of the mixture of complex alkali sulfates present, and (b) their thermal-stability limits. The extreme width of this temperature band is approximately 400F, or corrosion due to the complex alkali sulfates may range from as low as 1000F to a maximum of 1400F, depending on the species present in the intermediate layer.

#### Corrective measures

Various methods of combatting corrosion of superheater and reheater tubes have been used or suggested, including the following:

1. The use of stainless steel shields to protect the most vulnerable tubes.
2. Coal selectivity and the grinding of coals to a finer size.
3. Improve combustion conditions, i.e., provide fast ignition, good mixing, and proper excess air.
4. Injection of additives (mainly magnesium- and calcium-bearing minerals) into furnace gases or directly on the tubes through sootblowers.

5. The use of more corrosion-resistant alloys and ceramic coatings on the most vulnerable superheater and reheater tubes.

Low temperature coal-ash corrosion is covered in Chapter 13.

### Fuel-oil ash

The ash content of residual fuel oil seldom exceeds 0.2%, an exceedingly small amount compared to that in coal. Nevertheless, even this small quantity of ash is capable of causing severe problems of external deposits and corrosion in boilers. Of the many elements that may appear in oil-ash deposits, the most important are vanadium, sodium, and sulfur. Compounds of these elements are found in almost every deposit in boilers fired by residual fuel oil and often constitute the major portion of these deposits.

### Origin of ash

As with coal, some of the ash-forming constituents in the crude oil had their origin in animal and vegetable matter from which the oil was derived. The remainder is extraneous material resulting from contact of the crude oil with rock structures and salt brines, or picked up during refining processes, storage and transportation.

In general, the ash content increases with increasing asphaltic constituents in which the sulfur acts largely as a bridge between aromatic rings. Elemental sulfur and hydrogen sulfide have been identified in crude oil, and simpler sulfur compounds are found in the distillates of crude oil including thio-esters, disulfides, thiophenes and mercaptans.

Vanadium, iron, sodium, nickel and calcium in fuel oil were probably derived from the rock strata but some elements such as vanadium, nickel, zinc and copper probably came from organic matter from which the petroleum was derived. Vanadium and nickel especially, are known to be present in organo-metallic compounds known as porphyrins which are characteristic of certain forms of animal life. Table 8 indicates the amounts of vanadium, nickel and sodium present in residual fuel oils from various crudes.

Table 8  
Vanadium, nickel and sodium content  
of residual fuel oils  
(parts per million by weight)

Source of Crude Oil	Vanadium	Nickel	Sodium
Africa			
1	55	5	22
2	1	5	—
Middle East			
3	7	—	1
4	173	51	—
5	47	10	8
United States			
6	13	—	350
7	6	2.5	120
8	11	—	84
Venezuela			
9	—	6	480
10	57	13	72
11	380	60	70
12	113	21	49
13	93	—	38

Crude oil as such is not normally used as a fuel but is further processed to yield a wide range of more valuable products. For example, in a modern U.S. refinery the average product yield, as a percentage of total throughput, is:

Gasoline	44.4
Lube oil fraction	16.4
Jet fuel	6.2
Kerosine	2.9
Distillates	22.5
Residual fuel	7.6

Virtually all metallic compounds and a large part of the sulfur compounds are concentrated in the distillation residue, as illustrated for sulfur in Table 9. Where low-sulfur residual fuel oils are required, they are obtained by blending with suitable stocks, including both heavy distillates and distillation from low-sulfur crudes. This procedure is also used occasionally if a residual fuel oil must meet specifications such as vanadium, or ash content.

Table 9  
Sulfur content in fractions of Kuwait crude oil

Fraction	Distillation Range, F	Total Sulfur % by Weight
Crude oil	—	2.55
Gasoline	124-253	0.05
Light naphtha	257-300	0.05
Heavy naphtha	307-387	0.11
Kerosine	405-460	0.45
Light gas oil	477-516	0.85
Heavy gas oil	538-583	1.15
Residual oil	588-928	3.70

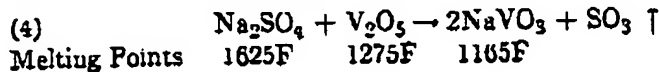
Source: Article by F. E. Hixon, Shell Refining and Marketing Co., Ltd., *Chemistry and Industry*, March 28, 1955, page 333.

### Release of ash during combustion

Residual fuel oil is preheated and atomized to provide enough reactive surface so that it will burn completely within the boiler furnace. The atomized fuel oil burns in two stages. In the first stage the volatile portion burns and leaves a porous coke residue, and in the second stage the coke residue burns. In general, the rate of combustion of the coke residue is inversely proportional to the square of its diameter, which in turn is related to the droplet diameter. Thus, small fuel droplets give rise to coke residues that burn very rapidly and the ash-forming constituents are exposed to the highest temperatures in the flame envelope. The ash-forming constituents in the larger coke residues from the larger fuel droplets are heated more slowly, partly in association with carbon. Release of the ash from these residues is determined by the rate of oxidation of the carbon.

During combustion, the organic vanadium compounds in the residual fuel oil thermally decompose and oxidize in the gas stream to  $V_2O_3$ ,  $V_2O_4$  and finally  $V_2O_5$ . Although complete oxidation may not occur and there may be some dissociation, a large part of the vanadium originally present in the oil exists as vapor phase  $V_2O_5$  in the flue gas. The sodium, usually present as chloride in the oil, vaporizes and reacts with sulfur oxides either in the gas stream or after deposition on tube surfaces.

Subsequently, reactions take place between the vanadium and sodium compounds with the formation of complex vanadates having melting points lower than those of the parent compounds, for example:



Excess vanadium or sodium in the ash deposit, above that necessary for the formation of the sodium vanadates (or vanadyl vanadates), may be present as  $\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{SO}_4$ , respectively.

The sulfur in residual fuel is progressively released during combustion and is promptly oxidized to sulfur dioxide ( $\text{SO}_2$ ). A small amount of sulfur dioxide is further oxidized to  $\text{SO}_3$  by a small amount of atomic oxygen present in the hottest part of the flame. Also, catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  may occur as the flue gases pass over vanadium-rich ash deposits on high-temperature superheater tubes and refractories.

### Oil-slag formation and deposits

The deposition of oil-ash constituents on the furnace walls and superheater surfaces has been a serious problem in recent years. This deposition, coupled with corrosion of superheater and reheater tubes by deposits, was largely responsible for the break in the trend towards higher steam temperatures that occurred in the early 1960's.

Practically all boiler installations are now designed for steam temperatures in the 1000-1015F range to minimize those problems and to avoid the higher capital costs of the more expensive alloys required in tubes, steam piping, and turbine for 1050-1100F steam conditions.

There are many factors affecting oil-ash deposition on boiler heat absorbing surfaces. These factors may be grouped into the following interrelated categories:

1. Characteristics of the fuel oil.
2. Design of the boiler.
3. Operation of the boiler.

#### Characteristics of fuel-oil ash

Sodium and vanadium are the most significant elements in the fuel oil because they can form complex compounds having low melting temperatures, 480-1250F, as shown in Table 10. Such temperatures fall within the range of tube-metal temperatures generally encountered in furnace and superheater tube banks of many oil-fired boilers. However, because of its complex chemical composition, fuel-oil ash seldom has a single sharp melting point, but rather softens and melts over a wide temperature range.

An ash particle that is in a sticky, semi-molten state at the tube-surface temperature may adhere to the tube if it is brought into contact by the gas flow over the tube. Even a dry ash particle may adhere due to mutual attraction or surface roughness. Such an initial deposit layer will be at a higher temperature than that of the tube surface because of its relatively low thermal conductivity. This increased temperature promotes the formation of adherent deposits. Thus, fouling will continue until the deposit-surface temperature reaches a level at which all of the ash in the gas stream is in a

Table 10  
Melting points of some oil-ash constituents

Compound	Melting Point, F
Aluminum oxide, $\text{Al}_2\text{O}_3$	3720
Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$	1420*
Calcium oxide, $\text{CaO}$	4682
Calcium sulfate, $\text{CaSO}_4$	2640
Ferric oxide, $\text{Fe}_2\text{O}_3$	2850
Ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$	895*
Nickel oxide, $\text{NiO}$	3795
Nickel sulfate, $\text{NiSO}_4$	1545*
Silicon dioxide, $\text{SiO}_2$	3130
Sodium sulfate, $\text{Na}_2\text{SO}_4$	1625
Sodium bisulfate, $\text{NaHSO}_4$	480*
Sodium pyrosulfate, $\text{Na}_2\text{S}_2\text{O}_7$	750*
Sodium ferric sulfate, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$	1000
Vanadium trioxide, $\text{V}_2\text{O}_3$	3580
Vanadium tetroxide, $\text{V}_2\text{O}_4$	3580
Vanadium pentoxide, $\text{V}_2\text{O}_5$	1275
Sodium metavanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 (\text{NaVO}_3)$	1165
Sodium pyrovanadate, $2\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$	1185
Sodium orthovanadate, $3\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$	1560
Sodium vanadylvanadates, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot \text{V}_2\text{O}_5$	1160
$5\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 11\text{V}_2\text{O}_5$	995

\* Decomposes at a temperature around the melting point.

molten state so that the surface is merely washed by the liquid without freezing and continued buildup.

In experimental furnaces it has been found that the initial rate of ash buildup was greatest when the sodium-vanadium ratio in the fuel oil was 1 to 6, but an equilibrium thickness of deposit ( $\frac{1}{8}$  to  $\frac{1}{4}$  in. thick) was reached in approximately 100 hours of operation. When the fuel oil contained more refractory constituents such as silica, alumina, and iron oxide in addition to sodium and vanadium, an equilibrium condition was not reached and the tube banks ultimately plugged with ash deposits. However, these ash deposits were less dense, i.e., more friable than the glassy slags encountered with a 1 to 6 sodium-vanadium fuel oil. Both the rate of ash buildup and the ultimate thickness of the deposits are also influenced by physical factors such as the velocity and temperature of the flue gases and particularly the tube-metal temperature.

In predicting the behavior of a residual oil insofar as slagging and tube-bank fouling are concerned, several fuel variables are considered including (1) ash content, (2) ash analysis, particularly the sodium and vanadium levels and the concentration of major constituents, (3) melting and freezing temperatures of the ash, and (4) the total sulfur content of the oil. Applying this information in boiler design is largely a matter of experience.

#### Boiler design

Generally speaking, progressive fouling of furnaces and superheaters should not occur if the tube-metal temperatures do not exceed 1000F. If such trouble is encountered, the solution can usually be found in improving combustion conditions in the furnace and/or modifying the sootblowing procedures.

Studies on both laboratory and field installations have shown that the rate of ash deposition is approximately



proportional to the velocity and temperature of the flue gases, and the concentration of oil-ash constituents in the flue gases. The geometry of the furnace and the spacing of tubes in the convection banks are selected in the design of a boiler to minimize the rate of deposition. It is common practice to use in-line tube arrangements with progressively wider lateral spacings for tubes located in higher gas-temperature zones. This makes bridging of ash deposits between tubes less likely and facilitates cleaning of tube banks by the sootblowers.

#### Boiler operation

Poor atomization of the fuel oil results in longer flames and frequently increases the rate of slag buildup on furnace walls which, in turn, makes it more difficult to keep the convection sections of the boiler clean. Completing combustion before the gases pass over the first row of tubes is especially important. Relatively large carbonaceous particles have a far greater tendency to impinge on the tubes than do the smaller ash particles. If these larger particles are in a sticky state, they will adhere to the tubes where oxidation will proceed at a slow rate with consequent formation of ash. Fouling from this cause is difficult to detect by inspection during boiler outages because the carbonaceous material has usually disappeared completely. It can generally be detected during operation since flames are usually long and smoky and sparklers may be carried along in the flue gases.

Regular and thorough sootblowing can have a decisive effect on superheater and reheater fouling. To be fully effective, however, sootblowing cycles should be

frequent enough so that ash deposits cannot build up to a thickness where their surfaces become semi-molten. If this point is reached, complete removal of the ash deposit can be very difficult because the sootblowers now have a dual task to perform: (1) to cool the surface of the deposit below its freezing temperature and (2) to shatter the now solid mass of slag and break its bond to the tube surface. In instances of extreme slagging, it is sometimes necessary to relocate sootblowers, install additional sootblowers to control deposition in a critical zone, or to use additives.

The boiler load cycle can also have a significant effect on the severity of slagging and superheater fouling. A unit that is base-loaded for long periods is more apt to have fouling problems on a borderline fuel oil than a unit that takes daily swings in load. In the latter instance, the furnace generally remains cleaner due to periodic shedding of slag, with the result that the gas temperatures through the superheaters are appreciably lower. This eases the burden on the sootblowers and goes a long way towards controlling ash-deposit formation in the superheater-reheater tube banks. Overloading the boiler, even for an hour or two a day, should be avoided, especially if excess air has to be lowered to the point where some of the burners are starved of air. The furnace is apt to become slagged and ash deposition creeps into the superheater and reheater tube banks.

#### Oil-ash corrosion

##### High-temperature corrosion

The sodium-vanadium complexes, usually found in oil-ash deposits, are corrosive when molten. The corrosion mechanism is probably one of accelerated oxidation of metal brought about by oxygen transfer to its surface by the constituents in the molten ash, accompanied by the removal by the ash of the normal protective oxide coating on the metal surface.

Corrosion can also be caused by sulfate attack, particularly when sodium (or some other) chloride is also present in the fuel oil, and this may occur at metal temperatures as low as 1000F. This type of corrosion is more apt to be encountered on boilers burning a low-vanadium fuel oil but containing several hundred ppm of sodium chloride. Even when the chloride content of the fuel oil is negligible, sulfate corrosion may still be severe when reducing or alternating oxidizing-reducing conditions prevail around the tubes.

A measurable corrosion rate can be observed over a wide range of metal and gas temperatures, depending on the amount and composition of the oil-ash deposit. Fig. 28 shows the combined gas and metal temperature effects on corrosion for a specific fuel oil composition of 150 ppm vanadium, 70 ppm sodium, and 2.5% sulfur. As the vanadium concentration of the fuel oil varies, the amount of corrosion, compared to a 150-ppm vanadium fuel, will increase or decrease according to the curve shown in Fig. 29.

The effect of the sodium level in the fuel oil is not quite so clear-cut because combustion conditions and the chloride content of the fuel oil may be controlling. The sodium content does, however, definitely affect the minimum metal temperature at which corrosion will be significant.

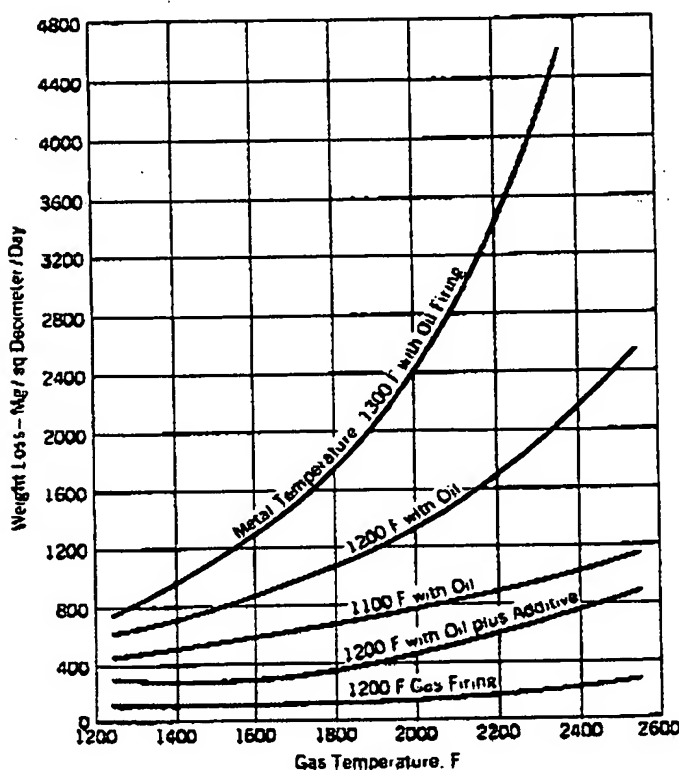


Fig. 28 Effect of gas and metal temperatures on corrosion of 304, 316, and 321 alloys in a unit fired with oil containing 150 ppm vanadium, 70 ppm sodium, and 2.5% sulfur. Test duration 100 hours.

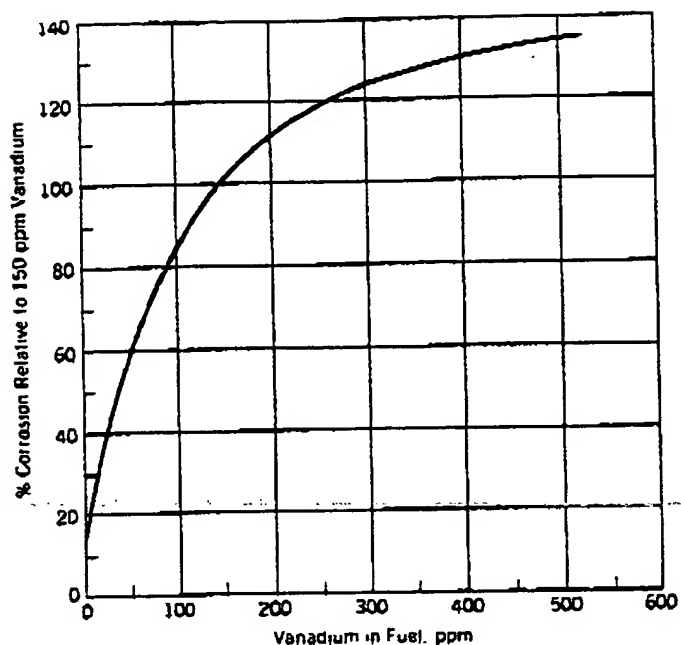


Fig. 29 Effect of vanadium concentration on oil-ash corrosion.

At the present time there does not appear to be any alloy that is immune to oil-ash corrosion. In general, the higher the chromium content of the alloy the more resistant it is to attack. This is the main reason for the use of 18Cr-8Ni alloys for high-temperature superheater tubes. High chromium contents, greater than 30%, give added corrosion resistance but at the expense of physical properties; 25Cr-20Ni has been used as a tube cladding but even this alloy has not provided complete protection. The presence of nickel in high-temperature alloys is needed for strength. High-nickel alloys may be fairly resistant to oil-ash attack under oxidizing conditions but they are liable to sulfide attack brought about by local reducing conditions or by the presence of chloride in the ash deposit. Since it is difficult to avoid such conditions entirely, high-nickel content of alloys may be of limited value. In any event, the higher material cost must be justified by longer life, which is not always predictable.

#### Low-temperature corrosion

In oil-fired boilers the problem of low-temperature corrosion resulting from the formation and condensation of sulfuric acid from the flue gases is similar to that previously described for coal firing.

Oil-fired boilers are more susceptible to low-temperature corrosion than are most coal-fired units for two reasons: (1) the vanadium in the oil-ash deposits is a good catalyst for the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  and (2) there is a smaller quantity of ash in the flue gases. Ash particles in the flue gas reduce the amount of  $\text{SO}_3$  vapor in the gas. Since oil has considerably less ash than coal, significant differences would be expected. Furthermore, coal ash is more basic than oil ash and tends to neutralize any acid deposited, oil ash generally lacks this capability.

Under certain conditions, oil-fired boilers may emit acidic particulates from their stacks that stain or etch

painted surfaces in the neighborhood of the plant. The acidic deposits or smuts are generally caused by metallic surfaces (air heaters, flues and stacks) operating well below the acid dew point of the flue gases or by soot which has absorbed sulfuric acid vapor in its passage through the boiler. Methods that can be used to prevent acid-smut emission include:

1. Minimize  $\text{SO}_3$  formation in the flue gases.
2. Neutralize  $\text{SO}_3$  in flue gases.
3. Maintain all surfaces in contact with the flue gases above about 250F and,
4. Completely burn fuel oil to eliminate soot particles.

#### Methods of control

The methods of control that have been used or proposed to control fouling and corrosion in oil-fired boilers are summarized in Table 11, but in every instance economics governs their applicability. There is no doubt that reducing the amount of ash and sulfur entering the furnace is the surest means of control, and that minimizing the effects of the ash constituents, once they have deposited on the tubes, is the least reliable. Since the severity of fouling and corrosion depends not only on the fuel-oil characteristics but also on boiler design and operating variables, a generalized solution to these problems cannot be prescribed.

Table 11  
Classification of methods for controlling fouling and corrosion in oil-fired boilers

	Fuel Oil Supply
Reduce amount of fuel ash constituents to the furnace	Selection Blending Purification
Minimize amounts of fuel ash constituents reaching heat transfer surfaces	Design Furnace geometry Tube bank arrangement Metal temperature Gas temperature Sootblower arrangement
Minimize effects of bonding and corrosive compounds in ash deposits	Operation Load cycle Sootblowing schedule Combustion—Excess air Additives Water washing

#### Fuel oil supply

Although fuel selection and blending are practiced to some extent in this country, it is done to provide safe and reliable handling and storage at the user's plant rather than to avoid fouling difficulties. Since the threshold limits of sodium, sulfur and vanadium are not accurately defined for either fouling or corrosion, utilization of these means of control cannot be fully exploited.

Processes are available for both the desulfurization and de-ashing of fuel oils. Water washing of residual fuel oil has been successfully applied to a few marine-type boilers, but it is doubtful that it will be widely used because only sodium and sediment, mainly rust and

sand, are removed by the process. Use of low-sulfur, low-ash crudes and desulfurized fuel oil is expected to increase (see also Chapter 18).

#### Fuel oil additives

The practice of water washing out of service and, to a limited extent, in service has been beneficial in overcoming some of the troubles experienced with present oil fuels. In addition, continued study of the problem has revealed another approach that is effective where the fuel-oil ash is most troublesome. In brief, the method involves adding to the fuel or furnace small amounts of materials that change the character of the ash sufficiently to permit its removal by steam or air sootblowers or air lances.

Additives are effective in reducing the troubles associated with superheater fouling, high-temperature ash corrosion, and low-temperature sulfuric acid corrosion. Most effective are alumina, dolomite and magnesia. Kaolin is also a source of alumina. Analyses of typical superheater deposits from a troublesome fuel oil, before and after treating it with alumina or dolomite, are shown in three bar graphs at the left in Fig. 30. The results for a different oil treated with magnesia are shown in the bar graph at the right.

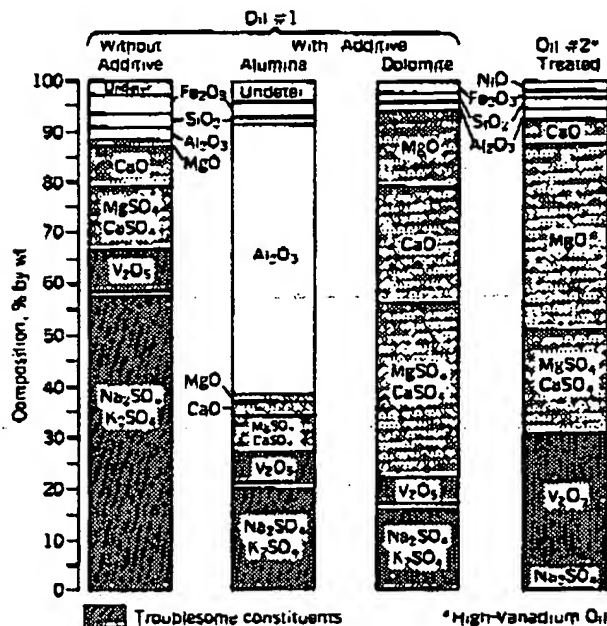


Fig. 30 Effect of fuel-oil additives on composition of oil-ash deposit.

The reduction of fouling and high-temperature corrosion is accomplished basically by producing a high-melting-point ash deposit that is powdery or friable and easily removed by sootblowers or lances. When the ash is dry, corrosion is considerably reduced.

Low-temperature sulfuric-acid corrosion is reduced by the formation of refractory sulfates by reaction with the  $\text{SO}_3$  gas in the flue-gas stream. By thus removing the  $\text{SO}_3$  gas, the dew point of the flue gases is sufficiently reduced to protect the metal surfaces. The sulfate compounds formed are relatively dry and easily removed by the normal cleaning equipment.

In general, the amount of additive used should be about equal to the ash content of the fuel oil. In some instances, slightly different proportions may be required for best results, especially for high-temperature corrosion reduction, in which it is generally accepted that the additive should be used in weight ratios of 2 or 3 to 1, based on the vanadium content of the oil.

Several methods have been successfully used to introduce the additive materials into the furnace. The one in general use consists of metering a controlled amount of an additive oil slurry into the burner supply line. The additive material should be pulverized to 100% through a 325-mesh screen (44 microns) for good dispersion and minimum atomizer wear.

For a boiler fired by a high-pressure return-flow oil system, it has been found advantageous to introduce the additive powders by blowing them into the furnace at the desired locations. The powder has to be 100% through a 325-mesh screen for good dispersion.

A third, and more recent method, is to introduce the additive as a water slurry through specially adapted sootblowers or lances. This method offers the advantage of applying the additive in exactly the location desired, with a possible reduction in the quantity required. Some caution should be observed with this system to prevent possible thermal shock (quench-cracking) damage to the hot tubes. The presence of chlorides in the water slurry, from either the water or the additive material, could possibly produce stress-corrosion cracking of austenitic tubing and should be considered.

The choice of the particular additive material depends on its availability and cost to the individual plant and the method of application chosen. For example, alumina

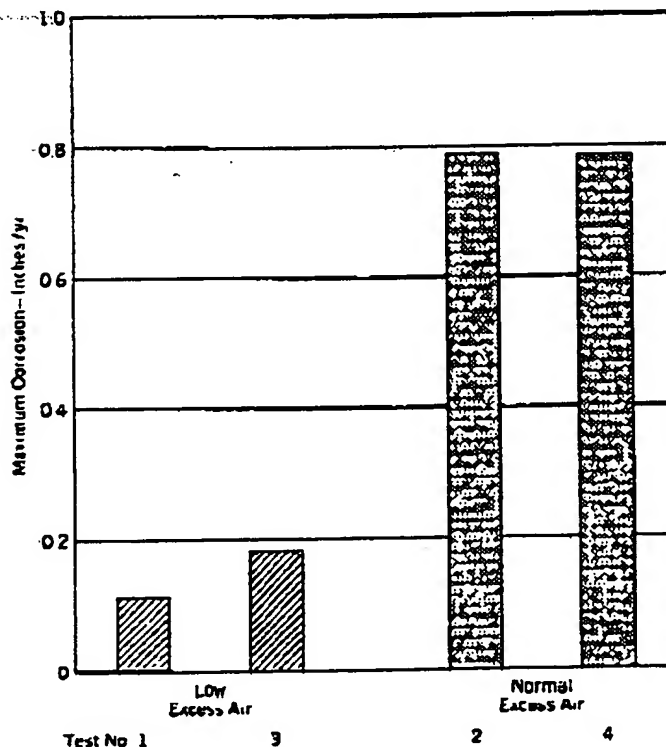


Fig. 31 Effect of low excess-air combustion on high-temperature oil-ash corrosion.



causes greater sprayer-plate wear than the other materials when used in an oil slurry.

The quantity of deposit formed is, of course, an important consideration for each individual unit from the aspect of cleaning. A comparison of the amounts of deposit formed with different additives shows that dolomite produces the greatest quantity because of its sulfating ability, alumina and kaolin form the least, and magnesia is intermediate. However, when adequate cleaning facilities are available, the deposits are easily removed, and the quantities formed should not be a problem.

#### Excess-air control

As mentioned previously the problems encountered in the combustion of residual fuels—high-temperature deposits (fouling), high-temperature corrosion, and low-temperature sulfuric-acid corrosion—all arise from the presence of vanadium and sulfur in their highest states of oxidation. By reducing the excess air from 7% to 1 or 2%, it is possible to avoid the formation of fully oxidized vanadium and sulfur compounds and, thereby, reduce boiler fouling and corrosion problems.

In a series of tests on an experimental boiler, it was found that the maximum corrosion rate of type 304 stainless steel superheater alloy held at 1250F in 2100F flue gas was reduced more than 75% (see Fig. 31) when the excess air was reduced from an average of 7% to a level of 1 to 2%. Moreover, the ash deposits that formed on the superheater bank were soft and powdery, in contrast to hard, dense deposits that adhered tenaciously to the tubes when the excess air was around 7%. Also, the rate of ash buildup was only half as great. Operation at the 1 to 2% excess air level practically eliminated low-temperature corrosion of carbon steel at all metal temperatures above the water dew point of the flue gases (Fig. 32). However, much of the beneficial effects of low excess-air combustion are lost if the excess air at the burner fluctuates even for short periods of time to a level of about 5%. Carbon loss values for low ex-

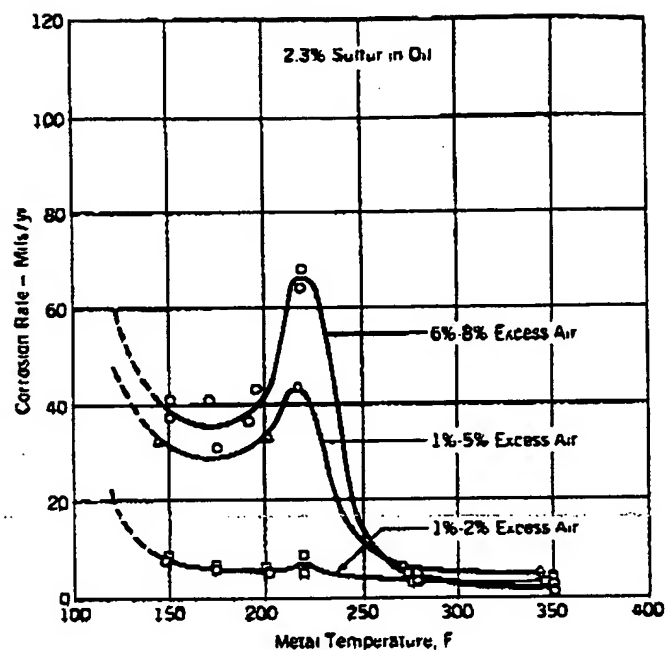


Fig. 32 Effect of excess air on low-temperature corrosion of carbon steel.

cess air were approximately 0.5%, which is generally acceptable for electric utility and industrial practice.

A number of large industrial boilers both in this country and in Europe have been operating with low excess air for several years. As a result, the benefits in reducing low-temperature corrosion are well established for units with steam temperatures of 1000F or less. However the benefits on high-temperature slagging and corrosion are not wholly conclusive. In any event, great care must be exercised to distribute the air and fuel oil equally to the burners, and combustion conditions must be continuously monitored to assure that combustion of the fuel is complete before the combustion gases enter the convection tube banks.

PATENT



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Application of:

JOHNSON et al.

Serial No.: 09/893,079

Filed: June 26, 2001

Atty. File No.: 3791-13

For: "LOW SULFUR COAL ADDITIVE  
FOR IMPROVED FURNACE  
OPERATION"

) Group Art Unit: 3749

) Examiner: Rinehart, Kenneth

) REVISED DECLARATION OF  
) RICHARD SCHLAGER

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

I, Richard Schlager, declare as follows:

1. That I am the Vice President of Contract Research and Development, and a shareholder, of ADA Environmental Solutions, LLC (hereinafter "ADA-ES"). ADA-ES is the assignee of the above-referenced patent application through an assignment executed on October 15, 2001, and recorded in the U.S. Patent and Trademark Office on October 22, 2001 at Reel 12664, Frame 0001. I am familiar with the above-referenced application. This Declaration is being submitted in connection with patent prosecution activities for the above-referenced patent application.

2. Based on a belief that byproducts of the steel industry may provide an effective fluxing agent for cyclone boilers, ADA-ES, in October, 1998, requested Physical Sciences, Inc., to calculate using computer modeling ash temperature and viscosity characteristics for a cyclone boiler

*Application No. 09/893,079*

using a mixture of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , which resembles various byproducts from the steel industry. The modeling was performed at a temperature of between 2000 and 2800°F, under reducing conditions and using blends of a coal ash and ADA-249 of 10, 15, 20, and 30 wt.% ADA-249. An analysis of the coals and the ADA-249 additive are attached hereto as Exhibit "B". A copy of the Purchase Order is attached hereto as Exhibit "C". The modeling results attached hereto as Exhibit "D" indicated that such an additive may be successful in a cyclone boiler. These tests were performed under obligations of confidentiality.

3. To confirm that the additive would be effective under the operating conditions of an actual cyclone boiler, ADA-ES contacted various utilities in an attempt to set up a test trial or demonstration of the additive. Attached hereto as Exhibit "E" is a sample of the letters sent to various utilities. The letter is to Sam Harman of the Tennessee Valley Authority and offers to perform a test using a formulation having the designation "ADA-249", which is a powdered blend of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , as an additive to the coal fed into a cyclone boiler. The letters were not sent out under an agreement of confidentiality.

4. One of the utilities contacted agreed to work with ADA-ES in conducting a demonstration. Attached hereto as Exhibit "A" is a copy of a Master Agreement between the Kansas City Board of Public Utilities (hereinafter "KCBPU") and ADA-ES, dated June 16, 1999 and executed by the parties on July 30, 1999 and July 20, 1999, respectively. The Master Agreement relates to the testing and sale of a low sulfur coal additive developed by ADA-ES under the designation "ADA-249."

5. One purpose of the Master Agreement was to provide ADA-ES with valuable testing of the ADA-249 product, and to potentially provide KCBPU with improved operation efficiency for their cyclone burners (or slag-type furnaces) when burning low sulfur coal.
6. Another purpose of the agreement was to provide ADA-ES with a revenue flow from the ADA-249 product.
7. ADA-ES is required under provision 201 of the Master Agreement, among other things, to provide and install a temporary system to inject a powdered fluxing agent into the coal pipe feeding the cyclone burners for the purpose of slag viscosity control.
8. Under provision 205 of the Master Agreement, the installation and startup of the fluxing agent injection system was to occur 16 weeks (112 days) after acceptance of purchase order.
9. Under provision 206 of the Master Agreement, a test period of 60 days after startup was to be conducted, with ADA-ES providing on-site testing services during the initial two weeks, including providing special test instrumentation to view cyclone outlets and slag tap and to measure furnace exit gas temperature.
10. The nature of ADA-249 is such that operational testing had to be done in a high capacity operating furnace, and had to be done for a substantial period of time.
11. KCBPU also incurred demonstration costs involved with the use of ADA-249. Sales under the Master Agreement, pursuant to provision 3.5 were conditional upon KCBPU recouping these demonstration costs through long term pricing guarantees from ADA-ES. As a further incentive and to reward KCBPU for allowing the low sulfur coal additive demonstration, KCBPU

also received other consideration from ADA-ES, until the costs of the demonstration paid by KCBPU were recouped.

12. The Master Agreement also contained, as exhibit D thereto, a confidential disclosure agreement, in which KCBPU agreed to maintain in strict confidence all confidential information disclosed by ADA-ES relating to ADA-ES proprietary iron fluxing technology.

13. Upon information and belief, approximately 142 tons of ADA-249 were delivered under the Master Agreement to the KCBPU Quindaro facility on or about April 17, 2000. This delivery was related to product ordered in a purchase order dated on or about March 1, 2000.

14. Upon information and belief, the startup of the powdered fluxing agent injection system occurred on or about April 18, 2000.

15. Upon information and belief, personnel from ADA-ES were present at the KCBPU Quindaro facility for the startup of the fluxing agent injection system. Furthermore, ADA-ES personnel were in close communication with KCBPU throughout the testing period, and returned to the facility on a regular basis through about May 17, 2001 to conduct follow-up observations of the system and further testing of the system.

16. Upon information and belief, ADA-ES routinely conducted follow-up inquiries regarding the performance of the low sulfur coal additive, and KCBPU understood that ADA-ES required information related to the performance of the low sulfur coal additive.

17. Upon information and belief, KCBPU communicated to ADA-ES what was considered unsatisfactory operation of the low sulfur coal additive.

18. ADA-ES has, subsequent to the work with KCBPU, performed demonstrations of the ADA-249 coal additive with at least two other facilities in order to prove operational effectiveness of ADA-249.

19. ADA-249 is delivered in the form of a dust having a  $P_{90}$  size of less than or equal to about 300 microns.

20. Upon information and belief, the composition of ADA-249 is as follows:

<u>Compound</u>	<u>% wt (dry basis of the additive)</u>
Iron	>50%
Mineralizer	>1.0%

21. Upon information and belief, the mineralizer includes at least 1.0 wt.% (dry basis of the additive) zinc, and ADA-249 contains a flow aid and abrasive material.

22. Upon information and belief, the iron contained in ADA-249 is in the form of a mixture of ferrus and ferric oxides, and contains about 10 wt.% (dry basis of the additive) wustite.

23. Upon information and belief, ADA-249 was used in the KCBPU demonstration as an iron-containing additive to coal-containing feed material. The iron-containing additive is contacted with the feed material and provided to a coal combustion chamber. At least a portion of the coal-containing feed material and iron-containing additive are melted to form a slag layer on at least a portion of a surface of the combustion chamber, whereby coal in the coal-containing feed material is captured by the slag layer and combusted. ADA-249 was used with a coal-containing feed material which comprises ash and less than about 1 wt.% (dry basis of the coal-containing feed material) sulfur, with the ash containing less than about 10 wt.% (dry basis of the ash) iron, and at

Application No. 09/893,079

least about 20 wt.% (dry basis of the ash) alkali. The ash contained at least about 15 wt.% (dry basis of the ash) calcium.

24. Upon information and belief, the feed material included coal particles entrained in an oxygen-containing gas, and the coal particles had a  $P_{90}$  size of less than or equal to about 0.25 inches.

25. Upon information and belief, the injection rate of ADA-249 additive into the combustion chamber ranged from about 10 to about 50 lb/ton coal. The blend rate was intentionally adjusted during the demonstration and results of different blend rates monitored.

26. I hereby declare that all statements made herein of my own are true and that all statements made on information and belief are believed to be true; and further, that the statements were made with the knowledge that willful false statements and the like, so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the subject application or any patent issuing thereon.

Date: 8-19-03

By: Richard Schlager  
Richard Schlager

# **EXHIBIT A**



# MASTER AGREEMENT

This Master Agreement is made and entered into as of June 16, 1999, by and between Kansas City Board of Public Utilities of Kansas City, Kansas, an administrative agency of the Unified Government of Wyandotte County/Kansas City, Kansas, (hereinafter referred to as "KCBPU") and ADA Environmental Solutions, LLC, a subsidiary of Earth Sciences, Inc., a corporation organized and existing under the laws of the State of Colorado and licensed to do business in Kansas, (hereinafter referred to as CONTRACTOR").

WHEREAS, KCBPU, from time to time will require various services;

WHEREAS, CONTRACTOR desires to and is able to provide KCBPU with said services, under the terms and conditions of this Master Agreement and any applicable documents;

NOW, THEREFORE, KCBPU and CONTRACTOR agree as follows:

## ARTICLE I. ACCEPTANCE & PAYMENT

- 1.1 SCOPE OF SERVICES - Upon issuance of a KCBPU "Purchase Order" form referencing this Master Agreement, CONTRACTOR shall perform such services as are delineated in the Purchase Order, and as may be set out in one or more Exhibits attached hereto.

KCBPU may from time to time, at its option, alter the scope of services in accordance with the provisions of section 1.4.

- 1.2 ACCEPTANCE - CONTRACTOR's commencement of work on any Purchase Order shall be an effective acceptance of any Purchase Order. Acceptance of any Purchase Order is subject to acceptance of the express terms contained in this Master Agreement and any Exhibits, and the specific Purchase Order in question. Any additional or different terms proposed by KCBPU or CONTRACTOR shall be without effect unless expressly accepted by both parties, in writing. In the event of a conflict between this Master Agreement and the language of any Purchase Order, this Master Agreement shall be controlling. In the event of a conflict between this Master Agreement or any Purchase Order and the language in any Exhibit, the Exhibit shall be controlling.

- 1.3 PRICE AND PAYMENT - Unless otherwise addressed in Article 3.1, KCBPU shall pay CONTRACTOR for the performance of services hereunder and under any applicable Purchase Order in accordance with the applicable Purchase Order:

CONTRACTOR shall submit a monthly invoice for the costs of services provided during the previous monthly period for the work specified hereunder and under any Purchase

Order. All invoices shall include applicable supporting documentation for verification of invoice amounts and all invoices shall include an itemized statement of the work performed and time spent. Unless otherwise addressed in Article 3.1, payments shall be made to the CONTRACTOR by KCBPU no later than thirty (30) days from the invoice date. An interest charge of 1-1/2% per month will be assessed on all late payments.

- 1.4 CHANGES - KCBPU shall at its option have the right to make any changes, including deletions, additions or modifications, in any services performed hereunder or under any Purchase Order and may direct CONTRACTOR to perform according to the changes made. If any such change causes an increase or decrease in the amount due CONTRACTOR, or the amount charged KCBPU, or the amount of time required by CONTRACTOR for the performance of any services, CONTRACTOR's compensation and/or time for performance shall be adjusted accordingly and KCBPU and CONTRACTOR shall make equitable adjustments in payments and charges as required. Adjustments in the compensation, if any, shall be based on the applicable prices, rates or reimbursable costs as set forth in this Agreement or any compensation schedule agreed to, in writing, by KCBPU and CONTRACTOR.

KCBPU must authorize all changes and requests for performance of additional services or the deletion of services in writing and give CONTRACTOR 30 days notice of such changes. Any unauthorized work performed or any unauthorized deletions performed shall be payable solely at KCBPU's option.

- 1.5 INSCRIPTION - Purchase Orders issued under this Agreement shall include the following statement on the face of the order:

The "Master Agreement" entered into as of June 16, 1999, shall govern this Purchase Order. Any pre-printed terms and conditions on this Purchase Order are hereby deleted, unless specifically accepted in writing by both parties."

- 1.6 PRESUMPTION OF INSCRIPTION - Notwithstanding 1.5 above, any Purchase Order not so inscribed shall be presumed to be governed by the provisions of this Master Agreement unless both parties agree in writing that this Master Agreement shall not apply to a particular Purchase Order.

## ARTICLE II. LIABILITY AND WARRANTY.

- 2.1 INDEMNIFICATION - CONTRACTOR shall fully defend, protect, indemnify and hold harmless KCBPU, its affiliates, directors, officers, employees and agents from and against all losses and liability and each and every claim, demand or cause of action including those arising out of contract or tort and any liability, costs, expense (including attorneys' fees and other costs incurred in the defense of KCBPU), on account of personal/bodily injury, including wrongful death, property damages, or breach of Agreement caused by, arising out of, or resulting from breach of Agreement or any negligent acts, omissions and/or fault of CONTRACTOR, its employees, agents or subcontractors, their employees and agents,

while engaged in the performance of any work hereunder, or the rendering of any services hereunder, or under any Purchase Order covered by this Master Agreement. Maximum CONTRACTOR liabilities will not exceed insurance coverage amounts.

CONTRACTOR shall at all times be considered an independent CONTRACTOR and shall not be considered at any time for any purpose to be a subcontractor, agent or employee of KCBPU.

CONTRACTOR shall direct and control its subcontractors, and shall have full responsibility for all services performed hereunder or under any Purchase Order, whether the services are performed by CONTRACTOR or its subcontractors, agents or assigns. CONTRACTOR shall be responsible to KCBPU and shall indemnify and hold harmless KCBPU, its affiliates, directors, officers, employees and agents for all services performed by, and for the acts, omissions or negligence of CONTRACTOR's subcontractors and all employees or agents of its subcontractors, and CONTRACTOR shall be responsible to and indemnify and hold harmless KCBPU, its affiliates, directors, officers, employees and agents for failure of CONTRACTOR's subcontractors to comply with the requirements of this Agreement, any Purchase Order, and all applicable laws, rules, and regulations, to the extent that CONTRACTOR would be responsible if performing the services itself.

The indemnification provided above by CONTRACTOR to KCBPU shall be extended by CONTRACTOR and insure to the benefit of any and all entities (partners, co-owners, or shareholders with KCBPU) which hold an ownership interest, in any way, in the premises on or in which the work or services are being performed by CONTRACTOR. The indemnification given these entities shall be equal to the indemnification given KCBPU by CONTRACTOR above.

- 2.2 LIMITATION OF LIABILITY - Neither KCBPU nor CONTRACTOR, their affiliates, directors, officers, agents, subcontractors, employees or assigns, shall be liable, whether arising out of contract, tort, strict liability, or any other cause or form of action, for loss of anticipated profits, loss by reason of plant or other facility shutdown, nonoperation or increased expense of operation, service interruptions, cost of purchased or replacement power, loss of use of capital or revenue, or for any special, incidental, or consequential loss or damage not specifically allowed herein.

This paragraph does not limit or affect CONTRACTOR's obligations under Paragraph 2.1 above.

- 2.3 WARRANTIES - CONTRACTOR warrants that it shall perform all services in a competent, careful, skillful and diligent manner when measured against the applicable professional standards recognized by CONTRACTOR's profession at the time of performance. CONTRACTOR shall comply with all applicable federal, state and local laws, ordinances, codes and regulations in performing its services. CONTRACTOR warrants that it, its employees, agents, subcontractors and assigns possess all requisite licenses and permits for their profession. If CONTRACTOR fails to meet this warranty,

CONTRACTOR shall, without additional compensation, correct, reperform or revise any defective work or services. In addition, CONTRACTOR shall reimburse KCBPU for any loss or damage, of whatever nature, which results from CONTRACTOR's, its employee's, agent's, subcontractor's, or assign's, failure to perform according to applicable professional standards or for any misrepresentation as to professional qualifications or ability to perform services. CONTRACTOR warrants that the services provided hereunder or under any Purchase Order, will conform to applicable Purchase Orders and that said services shall be free from defects and fit and sufficient for the purpose intended.

These warranties shall be in addition to all other warranties, express, implied or statutory. Payment for, inspection of, receipt of, or acceptance of services hereunder or under any Purchase Orders shall not constitute a waiver of any breach of warranty.

2.4 NON-WAIVER - Failure of either party to insist upon or enforce, in any instance, strict performance by the other party of any of the terms or provision of this Agreement or any Purchase Orders, including those relating to compensation or to the exercise of any right herein confirmed, shall not be construed as a waiver or relinquishment of any right either party may have to assert or rely upon the terms and conditions of this Agreement or any Purchase Orders in the future.

2.5 INSURANCE - CONTRACTOR shall maintain, at its expense, insurance coverage of the kind, type and in the limits specified in Exhibit B. The insurance specified in Exhibit B shall be the minimum insurance required of CONTRACTOR by KCBPU. CONTRACTOR shall be responsible for providing any additional insurance necessary to protect CONTRACTOR's and KCBPU's interests and provide for CONTRACTOR's performance hereunder, particularly under Article II. CONTRACTOR shall, upon request, furnish KCBPU with certificates of insurance evidencing the required coverage, and shall also furnish, upon request, copies of the insurance policies in effect.

### ARTICLE III. MISCELLANEOUS PROVISIONS

3.1 ASSIGNMENT AND SUBCONTRACTING - Payments made hereunder or under any Purchase Order may be assigned by CONTRACTOR to Wells Fargo Business Credit, Inc., KCBPU agrees to execute a letter similar to the letter in Exhibit C authorizing the assignment. No invoices may be rendered by anyone other than CONTRACTOR without the written permission of KCBPU.

CONTRACTOR shall not enter into any subcontracting agreement without KCBPU's written approval. Approved Subcontractors are listed in Exhibit E. Prior to approval, KCBPU may require submission of any subcontracting agreement(s) to KCBPU for approval. KCBPU's approval of any subcontracting agreement or the terms and conditions of any such subcontracting agreement shall not alter the provisions of this Agreement or any Purchase Order in any form or manner. CONTRACTOR's obligations, liabilities and duties under this Agreement and any Purchase Order accepted by CONTRACTOR shall remain unaffected. Nothing in any subcontracting agreement shall

constitute or create a contractual relationship between a subcontractor of CONTRACTOR and KCBPU. KCBPU shall have no responsibility or obligation to pay any sums to any subcontractors unless said subcontractor executes a contract with KCBPU. Possible subcontractors include employees of ADA Technologies, [REDACTED], and [REDACTED] (Draftsman) as listed in Exhibit E.

- 3.2 **TERMINATION** - KCBPU shall at any time have the absolute right to cancel this Agreement or any Purchase Order, in whole or in part, for any reason, upon thirty- (30) days written notice and upon payment to CONTRACTOR for services rendered through the time of cancellation. Upon notice of cancellation, CONTRACTOR shall cease performance of any services hereunder or under any Purchase Order accepted by CONTRACTOR, except as may be necessary to effect the cancellation. CONTRACTOR shall take any action necessary for cancellation of any services as may be reasonably directed by KCBPU. Upon cancellation, the obligations of KCBPU and CONTRACTOR to one another shall cease, except for such obligations which, by their nature, or by Agreement, survive completion of any services hereunder or under any Purchase Order. If only a portion of the service is canceled by KCBPU, CONTRACTOR shall continue to perform all other services not canceled, and as to the portions of the services not canceled, the Agreement and Purchase Order shall remain in full force and effect. In no event shall KCBPU be liable to CONTRACTOR for any anticipated profits on any portion of the services canceled by KCBPU nor for any other sums except as set forth herein or under a Purchase Order.
- 3.3 **CONFIDENTIALITY** - Any information, documents, correspondence or any form of communication noted as confidential belonging to KCBPU shall be considered confidential and CONTRACTOR shall not disclose such confidential information to anyone, without the express written consent of KCBPU or as may be required by law. KCBPU acknowledges the attached confidentiality agreement and agrees that in addition to other confidential information this confidentiality agreement applies to all costing information provided to KCBPU by CONTRACTOR.
- 3.4 **PUBLIC ANNOUNCEMENT** - CONTRACTOR shall not make any announcement or release of any information concerning any services under this Agreement or any Purchase Order unless such announcement or release has been submitted to and approved in writing by KCBPU. Such KCBPU approval shall not be unreasonably withheld.
- 3.5 **LONG TERM PRICING PROTECTION AND RECOUPING KCBPU DEMO COST** - As a reward to KCBPU for support in getting ADA-249 demonstrated and help from KCBPU in obtaining other ADA-249 applications at other non-KCBPU stations, CONTRACTOR will provide long-term ADA-249 pricing guarantees and provide a mechanism for KCBPU to recoup their demonstration costs.

After the demonstration CONTRACTOR will be the exclusive supplier of the Fe material (ADA-249) to KCBPU. Costs of the Fe material, which are considered confidential per the attached agreement, will be made known to KCBPU from CONTRACTOR. [REDACTED]

Also, as a further incentive and to reward KCBPU for allowing the Fe application demonstration [REDACTED] until the costs of the demonstration paid by KCBPU are recouped [REDACTED] payments will cease upon contract termination by either party or after KCBPU's demonstration costs are recovered.

- 3.6 APPLICABLE LAW - The definition of terms used, interpretation of this Agreement and rights of all parties shall be construed under and governed by the laws of the State of Kansas and venue, shall be proper only in the State and Federal courts located in Kansas.
- 3.7 FORCE MAJEURE - Neither party shall be considered in default of the performance of its obligations under this Agreement to the extent that the default arises out of and the performance is prevented or delayed by any force majeure, including but not limited to strikes, fires, accidents, acts of God or other causes beyond the control of either party. However, when either party, through its negligence or willful act, causes damages combined with or concurrent with any force majeure excluded hereunder, said party shall be liable for the damages occurring which would not have occurred but for its own conduct or omission.
- 3.8 NOTICES - All written notices required or permitted to be given under this Agreement or any Purchase Order shall be delivered to the address below, by delivery in person, telegram or United States mail, first class postage, prepaid. No notice shall be effective until received by the party to whom the notice is addressed.

Kansas City Board of Public Utilities  
Quindaro Power Station  
3601 North 12<sup>th</sup> Street  
Kansas City, KS 66104

ADA Environmental Solutions, LLC  
8100 South Park Way, B-2  
Littleton, CO 80120

- 3.9 TERM - This Agreement may be canceled by either party at any time by giving thirty (30) days written notice to the other party. If not canceled by either party, it is deemed renewed and continuing month to month.

- 3.10 SEVERABILITY - Every part, term or provision of this Agreement is severable from the others. Notwithstanding any possible future finding by duly constituted authority that a particular part, term or provision is invalid, void, or unenforceable, this Agreement has been made with the clear intention that the validity and enforceability of the remaining parts, terms and provisions shall not be affected thereby.
- 3.11 INTEGRATION - There are no understandings between the parties hereto as to the subject matter of this Agreement, including its Appendices and Exhibits, other than as set forth herein. All previous communications concerning the subject matter of this Agreement, either oral or written, are hereby abrogated and withdrawn and this Agreement, including its Appendices and Exhibits, constitutes the entire Agreement between the parties. Neither this Agreement or its Appendices and Exhibits may be changed or modified except by a writing executed by duly authorized representatives of each party. This Agreement incorporates Exhibit A - Project Specifications, Exhibit B - Minimum Insurance Coverage to be Maintained by the CONTRACTOR, Exhibit C - Wells Fargo Example Letter, Exhibit D - Confidential Disclosure Agreement, and Exhibit E - Rate Sheet.
- 3.12 HEADINGS- Paragraph headings are for the convenience of the parties only and are not to be construed as part of this Agreement.
- 3.13 SAFETY - All work performed by CONTRACTOR under this Agreement or any Work Authorization form shall be carried out in a safe and reasonable manner and CONTRACTOR shall be solely responsible for job safety.

CONTRACTOR shall comply with all federal, state and local safety laws, rules and regulations and any safety procedures customarily recognized by other contractors performing the same or similar work.

Failure of CONTRACTOR to comply with any safety rule or regulation shall be cause, at KCBPU's option, for immediate termination and/or suspension of this Agreement and any work being performed hereunder or under any Work Authorization. If KCBPU suspends any work, KCBPU shall have sole discretion to determine when a safety violation has been corrected and work can re-commence.

In addition, should KCBPU present CONTRACTOR, at any time during the existence of this agreement, with any safety manuals, safety rules, regulations or guidelines adopted by KCBPU, CONTRACTOR shall comply with said safety regulations, safety rules, manuals or guidelines during all work or services performed by CONTRACTOR under this Agreement or any Work Authorization issued by KCBPU.

- 3.14 EQUIPMENT - CONTRACTOR shall provide, at its expense, tools, machinery and implements necessary to perform all services hereunder or under any Purchase Order. Any of the above equipment, tools, or machinery or implements are the sole responsibility of CONTRACTOR and CONTRACTOR shall be liable for any damages or costs arising out of the use of said equipment.

IN WITNESS WHEREOF, the parties hereto have entered into this Agreement as of the date stated above.

Kansas City Board of Public Utilities

Approved (C.G.):  
[Signature]  
7-26-99

BY:

[Signature]

TITLE:

General Manager

ADA Environmental Solutions, LLC

BY:

[Signature]

TITLE:

V.P.



## EXHIBIT A - PROJECT SPECIFICATION

### 100. GENERAL REQUIREMENTS

#### 101. NAME OF PROJECT Demonstrate ADA-249 (Fe) fluxing application at KCBPU.

### 102. GENERAL CONDITIONS

- 102.1. The CONTRACTOR shall furnish pricing to provide all supervision, labor, materials, and equipment as indicated in these specifications.
- 102.2. The pricing shall include all travel and living expenses required for CONTRACTOR personnel.
- 102.3. The work shall be performed per the attached Scope of Work set forth below.
- 102.4. CONTRACTOR shall begin work after acceptance of bid and signing of Agreement and in accordance with this Exhibit A.
- 102.5. Any work which is rejected by the PURCHASER, due to a stated defect or nonconformance with Construction Documents, shall be satisfactorily corrected or replaced promptly. No other work shall be performed until the rejected work has been corrected or replaced.
- 102.6. CONTRACTOR shall maintain a clean work area, free of obstructions to normal travel, fire hazards, etc.

### 103. CHANGES IN THE WORK

- 103.1. PURCHASER shall have the right to make any changes in the WORK, the Agreement price being increased or decreased accordingly. No claim for changes in the WORK involving additional cost shall be allowed unless each specific change shall have been ordered in writing by PURCHASER.
- 103.2. All claims for payments for additions to the Agreement price shall be shown separately on CONTRACTORS invoices, and not included with amounts applicable to the main Agreement price. Further, any invoices covering additions to the Agreement must refer to the specific Change Order or similar written authorization issued by PURCHASER, approving such additions, and will not be honored unless such reference is included.

104. MATERIALS AND WARRANTY

104.1. Materials shall be the best of their respective kinds. Rental equipment may be used.

104.2. CONTRACTOR warrants:

104.3. That the WORK will conform to the specifications, drawings, samples and other description furnished or specified by PURCHASER pursuant to this Agreement and will be of good material and workmanship and free from defect.

104.4. That the WORK will be suitable for the purpose intended by PURCHASER.

104.5. That the WORK will be of the best quality and satisfactory to the PURCHASER's needs.

104.6. In addition to the foregoing, CONTRACTOR agrees, promptly and at his own expense, either to remedy any part of the WORK which during the first year of actual use in service proves defective or otherwise unsuitable for the aforesaid purposes, or to replace such part of the WORK by shipping to PURCHASER a new part under the same terms as apply hereunder to the shipment of the original part. A similar warranty shall apply to any replacement parts. Any part of the WORK shall be considered defective or otherwise unsuitable if it shall not comply with the Agreement, or if, among other things, it shall develop an undue amount of noise, vibration, heating, deterioration, strain or wear during the first year of actual use in service, provided that said equipment be kept in good condition and be properly operated during said year. If CONTRACTOR does not remedy and/or replace any such work within a reasonable time after written notice by the PURCHASER, PURCHASER may remedy and/or replace it at CONTRACTOR's expense.

104.7. CONTRACTOR shall be responsible for completely fulfilling all performance specifications contained in the Agreement and his compliance with any material or design specifications, even though furnished by PURCHASER, shall not alter or diminish such responsibility.

104.8. CONTRACTOR agrees that any and all warranties stated in this section shall be in addition to all other warranties set forth in section 2.3 of the Agreement.

105. SAFE WORK PRACTICES

The following shall apply as appropriate:

105.1. Discovery of a hazardous substance:

- 105.2. The CONTRACTOR, in the performance of the work, shall be responsible upon the discovery of any material or substance in which he or his employee believes or suspects that the material is a hazardous substance shall immediately cease all activity in and around the suspected work area. The CONTRACTOR shall then, upon discovery, inform the plant superintendent or his representative of the condition and upon consultation, a resolution of the problem will be made. The CONTRACTOR will be authorized to resume work after the problem has been resolved to PURCHASER's satisfaction.
- 105.3. Personnel safety:
- 105.4. CONTRACTOR shall be responsible for the safety of personnel and will employ adequate work methods to avoid risk of bodily harm to any persons or risk of damage to any property. CONTRACTOR shall continuously inspect all work, materials, and equipment, and shall be responsible for discovery, determination, and correction of any unsafe conditions.
- 105.5. Eye Protection:
- 105.6. CONTRACTOR shall be responsible for maintaining and enforcing the wearing of eye protection of each of his employees and subcontracted employees, who are under CONTRACTOR'S direction, while doing work at any of KCBPU's solid fuel fired generating stations. Eye protection shall conform to ANSI Z87.1-1989 specification. (Eye protection is usually not required in buildings and rooms which are environmentally controlled).
- 105.7. Emergency Planning:
- 105.8. Emergency procedures and exiting of the work place in case of fire and other disasters shall be given due consideration and planning prior to the start of the project. Appropriate emergency telephone numbers will be posted in a conspicuous area and emergency plans and procedures will be available to the work force.
- 105.9. Availability of Material Safety Data Sheets (MSDS):
- 105.10. All chemicals brought on to the work site shall have the appropriate MSDS on file at CONTRACTOR FIELD OFFICE at this site. Copies of MSDS's shall be submitted to the plant superintendent or his representative of all chemicals brought on site with known or suspected acute or chronic health hazard effects.
106. DEFINITIONS
- 106.1. Wherever the term "CONTRACTOR" is used it shall be construed to mean "ADA Environmental Solutions, LLC."

106.2. Wherever the term "PURCHASER" or "Company" is used it shall be construed to mean "KCBPU Energy Company."

## 200. TECHNICAL REQUIREMENTS

### 201. Scope of Work

The CONTRACTOR is to provide and install a temporary system to inject a powdered fluxing agent into the coal pipe feeding the cyclone burners for the purpose of slag viscosity control.

CONTRACTOR shall provide a pneumatic transfer system for rail car unloading, a vent filter receiver and appurtenances, a rotary feeder, blower and piping to distribute the reagent into the coal pipes.

### 202. Design Criteria.

#### 202.1 Additive qualities.

Iron based

Non-toxic

#### 202.2. Operating parameters.

Over entire unit MW load and temperature range.

#### 202.3. Mode of operation.

Manual by PURCHASER's plant operators. Rotary feeder calibration curves provided by CONTRACTOR

#### 202.4. Rail car unloading system.

The CONTRACTOR shall supply a portable rail car unloading system that will consist of a receiving pan that will be positioned manually (with forklift) beneath the rail car hopper. A portable pneumatic conveying unit including blower and flexible discharge hose will be used to convey the material to the filter receiver with a high capacity hopper for storage of at least four hours of material.

#### 202.5. Reagent feed system

The CONTRACTOR shall supply a dilute phase pneumatic conveying system consisting of a ~~\_\_\_\_\_~~, check valves and controls.

203. CONTRACTOR Responsibility  
The CONTRACTOR is responsible to provide the following:-

- 1) Rail car unloading system.
- 2) Reagent feeder and pneumatic conveying system.
- 3) All engineering, labor and supervision for the installation of equipment.
- 4) All startup services.
- 5) Two weeks of initial testing services including labor and test instrumentation.
- 6) Training of PURCHASER's operators.
- 7) Maintenance support during the test period.
- 8) All parts and replacement equipment during test period.

204. PURCHASER Responsibility.  
The PURCHASER shall be responsible to provide the following:

- 1) 480v 60amp electrical supply to blower and rotary feeder.
- 2) 110v 30amp electrical supply to control panel.
- 3) Unloading of delivered equipment including providing crane and forklift as required.
- 4) Foundation and anchoring for filter receiver and blower.
- 5) Assembly of rail car unloading system.
- 6) Installation and assembly of filter receiver and all appurtenances.
- 7) [REDACTED]
- 8) Installation of injection piping and flow proportioning splitter valve.
- 9) Structural support steel for piping and conduit.
- 10) Rail car management and logistics at the plant.
- 11) Unloading reagent from rail cars.
- 12) Operation of the system after start-up and initial check-out.
- 13) Labor support for periodic system maintenance.

205. Installation and startup schedule  
The startup of the fluxing agent injection system will be 16 weeks after acceptance of purchase order.

206. Test period  
The fluxing agent injection system will be evaluated over a 60 day period after start-up. The CONTRACTOR shall provide on-site testing services during the initial two weeks including providing special test instrumentation to view cyclone outlets and slag tap and to measure furnace exit gas temperature.

The PURCHASER can terminate the test at any time with written notification to CONTRACTOR.

300. PRICING

300.1. Equipment

PURCHASER shall pay CONTRACTOR'S cost for equipment (including filter receiver, level indicators, rotary feeder valve, blower, piping, controls, rail car unloading system, etc.). Estimated cost for the uninstalled equipment not including shipping is [REDACTED]

300.2. Chemicals Purchase

The price for PURCHASER to purchase demonstration quantities of ADA-249 from CONTRACTOR [REDACTED]

300.3. Engineering, installation supervision, startup labor, and miscellaneous expenses  
PURCHASER shall pay CONTRACTOR for engineering, installation supervision, and labor and other costs related to the installation of the system, which shall be billed on a time and material basis per ADA-ES Standard Rates, which may be found in Exhibit E. The estimated cost for labor and expenses is [REDACTED]

## EXHIBIT B – MINIMUM INSURANCE COVERAGE TO BE MAINTAINED BY THE CONTRACTOR

Prior to starting work, Contractor shall procure and maintain in force, Workers' Compensation Insurance and Employer's Liability Insurance in full compliance with the laws of the State of Kansas. Comprehensive General Liability Insurance on an occurrence basis with contractual coverage and Automobile Liability Insurance, including owned, non-owned and hired automobile coverage and such other insurance, to the extent required by the Contract Documents for Contractor's Work.

Contractor's Commercial General and Automobile Liability Insurance, shall be written for not less than limits of Liability as follows:

- a. General Liability:
  - General Aggregate: \$ 2,000,000
  - Products-Completed Operations Aggregate: \$ 2,000,000
  - Personal & Advertising Injury: \$ 1,000,000
  - Each Occurrence: \$ 1,000,000
  - Fire Damage (Any One Fire): \$ 50,000
  - Medical Expenses: \$ 5,000
  - Professional Liability: \$ 1,000,000
  - Pollution Liability (Sudden and Accidental) \$ 1,000,000
- b. Certificates:

The Commercial General Liability coverage box and the Occurrence box, both must be marked with an "X" as included. The General Aggregate must be on a Per Project Basis and so noted on the Certificate of Insurance. In addition the Certificate must also indicate that KCBPU is an Additional Insured.
- c. Automobile Liability limits:
  - Combined Single Limit: \$ 1,000,000
  - (Bodily Injury and Property Damage Combined)

Regarding the Certificates: Coverage must include All Owned, Non-Owned and Hired Vehicles. The "Any Auto" box on the Certificate must be marked with an "X", as included.

- d. Coverage shall be written on a Commercial General and Automobile Liability form and must include Contractual Liability as applicable to the Contractors obligations.

The policies shall contain a provision that coverage is afforded under the policies will not be canceled or non-renewed until at least ten (10) days prior written notice has been given to KCBPU.

Contractor shall be responsible for providing insurance for all it's property, tools & equipment used at the job site. This includes all owned, leased, rented or borrowed equipment.

#### WORKERS COMPENSATION AND EMPLOYERS LIABILITY INSURANCE:

Each Accident:	\$ 100,000
Disease Policy Limit:	\$ 500,000
Disease Each Employee:	\$ 100,000

All job site personal must be covered by Workers Comp insurance. This requirement applies to Sole Proprietorships, Partnerships, Corporations, and any, Individual Employer, Corporate Officer or Working Partner.

The Workers Comp Certificate must specifically state "10 days notice prior to cancellation will be given to KCBPU."



# EXHIBIT C – WELLS FARGO EXAMPLE LETTER

WELLS  
FARGO

Wells Fargo Business Credit, Inc.  
2460 W. 26th Avenue, Suite C-120  
PO Box 11099  
Denver, Colorado 80211-1099  
303 433-9300  
303 433-2540 Fax

July 20, 1999

Dear Sir or Madam:

Your vendor, ADA Environmental Solutions LLC ("ADA") has entered into an Account Purchase Agreement with Wells Fargo Business Credit, Inc. ("WFBCI") pursuant to which ADA has assigned and sold all rights to payments, including rights to payment from you, to WFBCI in order to facilitate ADA's financing needs.

ADA has presented us with invoice number \_\_\_\_\_ for purchase which invoice is payable by ADA for \_\_\_\_\_.

In order for WFBCI to consider this account payable by you for purchase, WFBCI needs your assurance that the services have been provided and that the progress payment will be made without offset or defense to WFBCI.

By signing below, you agree that you are giving the assurances we have requested in this letter on behalf of \_\_\_\_\_ and that payment will be made within \_\_\_\_\_ days of the invoice date without offset or defense to WFBCI. You also represent that you understand that WFBCI is relying on your representations in making its decision whether or not to purchase the account and fund money on the account.

Please return a copy of this letter with an authorized signature if the foregoing is agreeable to the \_\_\_\_\_.

Yours very truly,

By: \_\_\_\_\_

Title: \_\_\_\_\_  
Wells Fargo Business Credit, Inc.

By: M. D. Durbin  
Title: President  
ADA Environmental Solutions LLC

Agreed and accepted:

BOARD OF Public Utilities

By: [Signature]

Title: General Manager

Authority: \_\_\_\_\_

Approved (Real)  
[Signature]  
7-20-99

# EXHIBIT D – CONFIDENTIAL DISCLOSURE AGREEMENT

## Confidential Disclosure Agreement

This is an Agreement by and between ADA Environmental Solutions, LLC. (hereinafter referred to as "ADA-ES"), having a place of business at 8100 SouthPark Way, B-2, Littleton, Colorado 80120 and Kansas City Board of Public Utilities (hereinafter referred to as "DISCLOSEE"), having a place of business at 3601 North 12<sup>th</sup> Street, Kansas City, KS, 66104.

1. ADA-ES agrees to disclose to DISCLOSEE information deemed proprietary and confidential relating to ADA-ES proprietary iron fluxing technology and other proprietary chemical application technologies for the sole purpose of DISCLOSEE's internal evaluation of the desirability of a demonstration of the technology. ADA-ES further agrees that any such information disclosed to DISCLOSEE in writing will be marked to indicate the confidential nature thereof, and any such information orally disclosed to DISCLOSEE will be referenced in writing by ADA-ES to DISCLOSEE within thirty (30) days of the oral disclosure.
2. DISCLOSEE agrees to maintain all information disclosed by ADA-ES in strict confidence, and not to disclose or use any information for any purpose other than the limited purpose set forth in Paragraph 1 above. DISCLOSEE further agrees that it shall not make copies of any materials provided by ADA-ES without the written authorization of ADA-ES, and that upon ADA-ES's request, it shall deliver to ADA-ES all materials comprising any information disclosed by ADA-ES.
3. DISCLOSEE's obligations set forth in Paragraph 2 above shall not extend to information:
  - (a) Which was already in the possession of the DISCLOSEE prior to receipt from ADA-ES, as evidenced by preexisting documentation; or
  - (b) Which is within the public domain or hereafter enters the public domain through no fault or action or failure to act on the part of DISCLOSEE; or
  - (c) Which is rightfully disclosed to DISCLOSEE by a third-party on a non-confidential and non-restricted basis; or
  - (d) Which is developed by or for DISCLOSEE independently and without reference to ADA-ES's information furnished hereunder by personnel having no access to such information of ADA-ES.

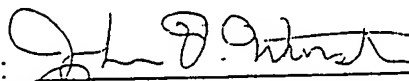
Information disclosed by ADA-ES to DISCLOSEE will not be deemed to fall within the above exceptions merely because such information can be found separately in an uncombined form, or is embraced by more general information, within DISCLOSEE's prior possession, within the public domain, or within information rightfully disclosed to DISCLOSEE on a non-confidential and non-restricted basis. DISCLOSEE's

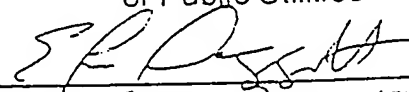
obligation under Paragraph 2 above shall continue until the subject matter in question falls within one or more of the exceptions of this Paragraph 3 or 2 years from effective date, whichever occurs first.

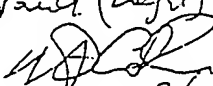
4. DISCLOSEE agrees to limit access to the information received from ADA-ES to its employees and consultants and only those employees and consultants who have "a need to know" in order to accomplish the limited purpose of this Agreement.
5. It is understood that no rights in, or license under any present or future information disclosed by ADA-ES to DISCLOSEE is either offered or granted to DISCLOSEE by this Agreement.
6. It is understood that ADA-ES assumes no liability to DISCLOSEE for loss or damage arising from DISCLOSEE's use of, or reliance upon, any information disclosed to DISCLOSEE pursuant to this Agreement.
7. This Agreement shall be governed by and construed in accordance with the laws of the State of Kansas. This Agreement supersedes any prior agreement between the parties relating to the subject matter of this Agreement, embodies the entire agreement of the parties, and may be modified only by a written agreement between the parties. This Agreement may not be assigned by the DISCLOSEE. ADA-ES may assign this Agreement.
8. Nothing contained in this agreement shall be construed to require KCBPU to violate the provisions of the Kansas Open Records Act as amended.

ADA ENVIRONMENTAL SOLUTIONS, LLC

DISCLOSEE: Kansas City Board  
of Public Utilities

By:   
Print Name: John F. Wurster  
Title: Vice President  
Date: 7/20/99

By:   
Print Name: E. Leon Daggett  
Title: General Manager  
Date: 7-30-99

  
7-30-99

## EXHIBIT E – ADA-ES RATE SHEET

# ADA Environmental Solutions, LLC

## Professional Rate Structure for 1999

Company	Category	Rate (\$/hour)
ADA Environmental Solutions	Principal Engineers	\$130
ADA Environmental Solutions	Senior Engineers	\$100
ADA Environmental Solutions	Specialists	\$70
ADA Environmental Solutions	Engineers	\$70
ADA Environmental Solutions	Technicians	\$55
ADA Environmental Solution	Admin. Assistant #1	\$50
ADA Environmental Solutions	Admin. Assistant #2	\$40
ADA Technologies	Senior Engineers	\$110
ADA Technologies	Research Engineers	\$75
ADA Technologies	Senior Technicians	\$80
ADA Technologies	Technicians	\$65
Apogee Scientific, Inc.	[REDACTED]	\$130.75
Apogee Scientific, Inc.	[REDACTED]	\$100
Apogee Scientific, Inc.	[REDACTED]	\$82.25
Apogee Scientific, Inc.	[REDACTED]	\$78
Apogee Scientific, Inc.	[REDACTED]	\$69.25
[REDACTED]	Draftsman	\$70

SHERIDAN ROSS  
A Professional Corporation  
ATTORNEYS AND COUNSELORS AT LAW  
1560 BROADWAY  
SUITE 1200  
DENVER, COLORADO 80202-5141

DAVID F. ZINGER  
CRAIG C. GROSETH  
TODD P. BLAKELY  
GARY J. CONNELL  
SABRINA C. STAVISH  
JOSEPH E. KOVARIK  
SUSAN PRYOR WILLSON  
LEWIS D. HANSEN  
ROBERT R. BRUNELLI  
DOUGLAS W. SWARTZ  
BRUCE A. KUGLER  
BRENT P. JOHNSON  
DANA HARTJE CARDWELL  
BENJAMIN B. LIEB  
BRADLEY M. KNEPPER  
MIRIAM DRICKMAN TRUDELL  
SCOTT R. BIALECKI  
KENNETH C. WINTERTON  
ROBERT D. TRAVER, Ph.D.  
CHRISTOPHER J. HUSSIN  
MARK L. YASKANIN  
MOLLYBETH R. KOICIALSKI

TELEPHONE (303) 863-9700  
FACSIMILE (303) 863-0223  
E-MAIL srlaw@sheridanross.com

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OF COUNSEL  
PHILIP H. SHERIDAN  
GILBERT E. ALBERDING\*  
\*MI, AL, IN Bar Only

TECHNICAL SPECIALISTS  
DENNIS J. DUPRAY, Ph.D.  
ANGELA K. DALLAS, Ph.D.

FACSIMILE COVER SHEET

DATE: September 18, 2002

Please deliver the following page(s) to:

Name: U.S. Patent Office  
ATTN: Kenneth Rinehart  
GROUP ART UNIT 3749

Facsimile Number: 1-703-872-9302

Our File Number: 3791-13

Total Number of Pages, including this cover page: 34

Sender's Name: Kenneth C. Winterton, Esq.

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## TRANSMISSION REPORT

(WED) SEP 18 2002 15:21

DOCUMENT #	3561683-859
TIME STORED	09. 18 15:12
TIME SENT	09. 18 15:12
DURATION	8' 42"
DESTINATION	P
DST. TEL#	30173791*13#17038729302
MODE	ECM
PAGE(S)	34PAGE(S)
RESULT	OK
DEPARTMENT	

## **EXHIBIT B**

TVA - Cyclone Ash Fluxing Project

	Kentucky Coal	Black Thunder	Additive
Constituent			
SiO <sub>2</sub>	45.0	38.2	1.0
Al <sub>2</sub> O <sub>3</sub>	19.0	17.1	0.2
TiO <sub>2</sub>	1.0	1.4	0.0
Fe <sub>2</sub> O <sub>3</sub>	27.0	5.1	70.0
CaO	2.2	23.4	15.4
MgO	0.8	5.0	3.0
K <sub>2</sub> O	2.1	0.4	0.6
Na <sub>2</sub> O	0.5	1.5	0.6
SO <sub>3</sub>	2.0	7.9	0.1
P <sub>2</sub> O <sub>5</sub>	0.2	1.0	0.1
ZnO			8.8
Total	99.8	99.0	99.7
T250	2310	2210	
Red ID	2000	2142	
Red FL	2320	2186	
Ox ID	2520	2211	
Ox FL	2590	2272	
Delta T (Ox FL - Red ID)	590	130	
Moisture	12.00	27.50	
Ash	8.00	5.90	
Volatiles	37.50	35.40	
Fixed Carbon	43.75	38.30	0.178
Sulfur	2.68	0.37	0.047
BTU/lb	11800.00	8790.00	
lbs SO <sub>2</sub> / MBTU	4.54	0.84	

## **EXHIBIT C**

# ADA Environmental Solutions, LLC

South West Business Center  
8100 SouthPark Way, B-2  
Littleton, Colorado 80120  
(303) 734-1727 Fax (303) 734-0330

## PURCHASE ORDER

The following number must appear on all related  
correspondence, shipping papers, and Invoices:

P.O. NUMBER: ES98-0342

Vendor:

Physical Sciences, Inc.  
20 New England Business Center  
Andover, MA

Shlp To:

ADA Environmental Solutions  
50 Nashua Rd  
Suite 112  
Londonderry, NH 03053

P.O. DATE	DATE REQUIRED	SHIP VIA	F.O.B. POINT	TERMS
10/12/98	ASAP	Email to <a href="mailto:johnc@adaes.com">johnc@adaes.com</a>	Vendor	Net 30

PROJECT/ACCOUNT NO.	VENDOR CONTACT	VENDOR CONTACT'S PHONE #
6112-01	Connie Senior	978-686-0003

QTY	PART #	DESCRIPTION	UNIT PRICE	TOTAL
1		Calculation of Ash Temperature/Viscosity Characteristics (See attached memo & data sheets for details)	1500.00	1500.00

Post-it Fax Note 7671		Date 10/12/98	# of pages 3
To Connie Senior		From John Comer	
Co/Dept.		Co.	
Phone # 978-689-0003		Phone #	
Fax # 978-689-3232		Fax #	

SPECIAL NOTE:

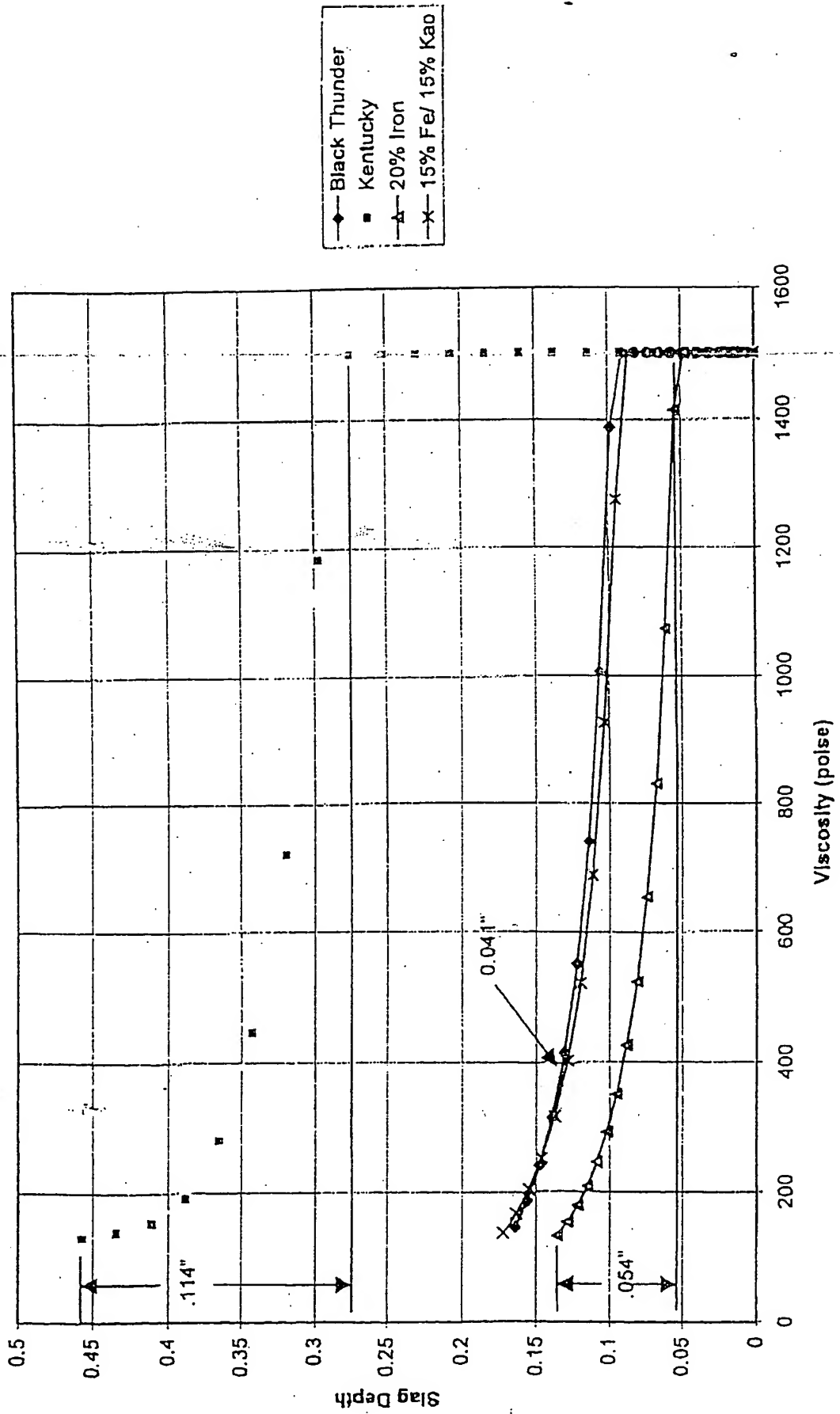
SUBTOTAL	\$1500.00
SALES TAX	
SHIPPING & HANDLING	
OTHER	
TOTAL	\$1500.00

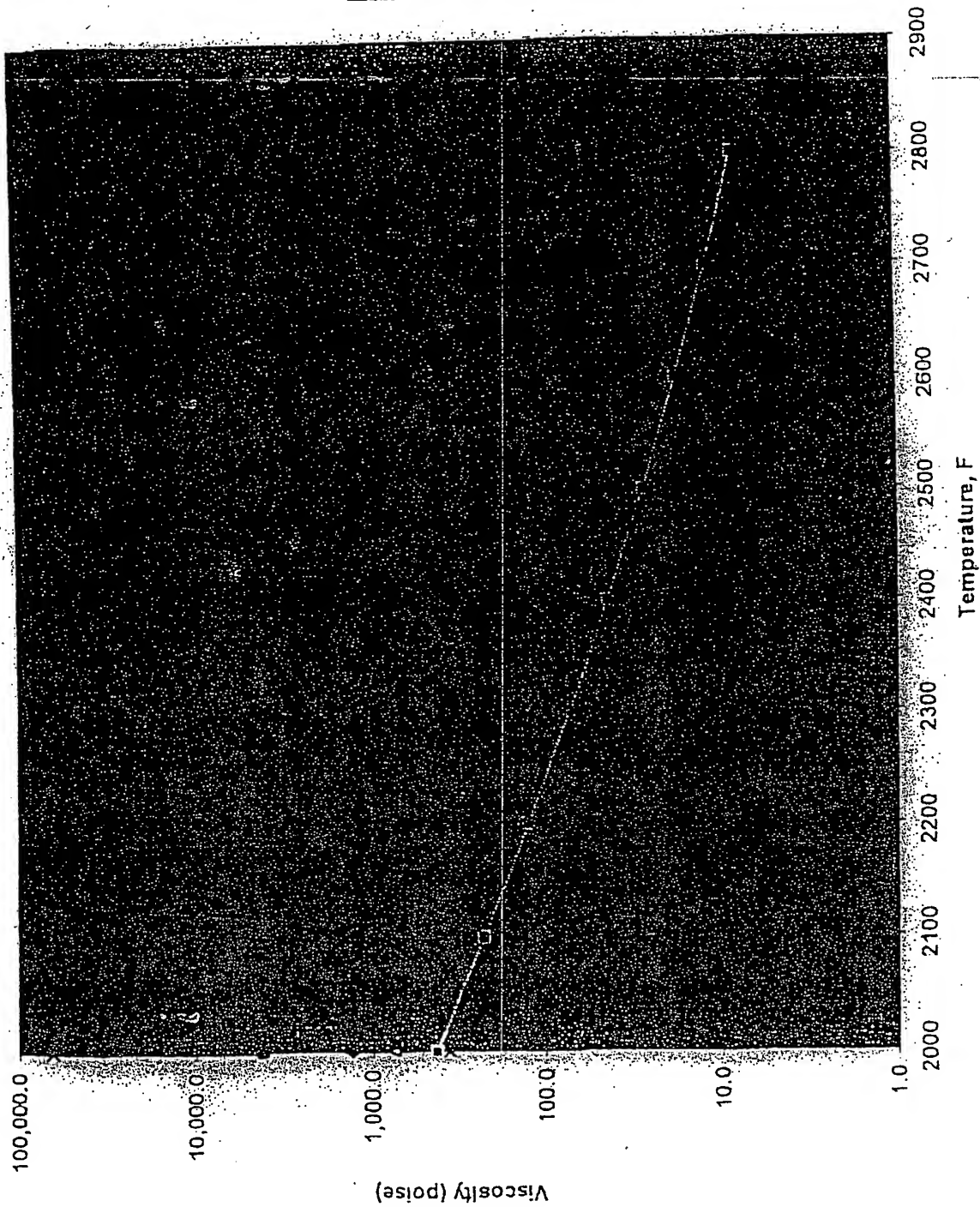
REQUESTED BY: J Comer

John P. Comer 10/12/98  
AUTHORIZED BY /DATE

## **EXHIBIT D**

# Cyclone Fluxing





- Black Thunder Red.
- △— Black Thunder Ox.
- \*— 15% Fe/15% Kao Red.
- ◆— 15% Fe/ 15% Kao Ox.
- Kentucky Red.
- ×— Kentucky Ox.



**EXHIBIT E**



November 6, 1998

Mr. Sam Harman  
Tennessee Valley Authority  
1101 Market Street, MR 3B  
Chattanooga, TN 37402

Dear Sam:

The purpose of this letter is to confirm our discussions regarding our inexpensive, optimized Fe blend for TVA, Paradise. It is called ADA-249.

As you are now finding at Paradise, firing cyclone boilers with low ash, high calcium fuels from the Powder River Basin presents a unique challenge. The symptoms include spouting from cyclones, high FEGT, heavy convection pass fouling, high carbon flyash, and increased loading at the ESP. You may be seeing some of these symptoms now.

These problems are caused because cyclone boilers are designed to operate with a coating of molten ash and burning fuel on the walls of each cyclone barrel. It is important that the coating is thick enough and of the proper viscosity to catch and hold a significant portion of the fuel as it enters the cyclone. This provides the proper residence time for good combustion and allows the ash in the coal to be directed to the slag taps and not into the convection pass where it eventually is removed as flyash. Coals which are generally considered suitable for combustion in a cyclone fired boiler have an ash T250 temperature of less than 2300°F and a wide temperature range (over 300°F) over which the cyclone slag remains sticky as well as molten. PRB coal generally has T250 very near this lower limit; however, it also passes through its viscosity range from solid to very low viscosity over a small temperature range (approximately 100°F). This means that the operation of the cyclones with a suitable sticky ash layer is almost impossible.

For this reason, TVA Paradise is planning to utilize iron pellets as a fluxing agent as you convert to PRB coal. ADA-ES agrees with TVA's conclusion that Fe should be utilized. Iron has other properties that make it attractive for use in fluxing PRB coal. Iron's fluxing properties are very dependent on the oxidation state of the iron. In a reducing atmosphere the iron produces ash with much higher viscosity. Literature suggests that the iron will be partially oxidized during the combustion process. This should produce an ash which has a slightly lower melting point, but with an extended high viscosity sticky region. The result should be substantially more combustion in the cyclones. This translates into significant fuel savings, increased bottom ash sales, less slagging and fouling and lower flyash LOI.

The addition of iron to the ash may also improve the radiation heat transfer properties of the furnace deposits. In typical PRB burning furnaces the radiation heat transfer is

substantially impeded due to the low emissivity of the deposits. Iron will help to increase the emissivity of the deposits and improve furnace heat transfer.

To help TVA Paradise, ADA-ES has obtained and modeled a very low cost, optimized iron blend, called ADA-249. Among other components, it is a blend of FeO and Fe<sub>2</sub>O<sub>3</sub>, and is in a powdered form that should allow for easy feeding into the belt leading to the boiler house. The powder will be easier to handle and due to its size distribution and the cyclone aerodynamics, should be retained in the cyclone for sufficient time to be incorporated into the ash layer.

Benefits of utilizing ADA-249 material include:

- Reduced costs compared to alternatives
- Easy to implement
- Easy to handle
- Reliable long term source
- Take advantage of ADA-ES expertise
- Assure combustion efficiency

For trial quantities ADA-ES can have the ADA-249 delivered to Paradise for \$ 50 per ton. Once efficacy is proven, a long-term supply arrangement can be developed. This should reduce costs to TVA by \$ 10 per ton. Yearly usage could approach 100,000 tons per year. Capital and engineering support will be provided by ADA-ES at standard rates.

Sam, this Fe source represents a great cost saving and efficiency enhancing opportunity for TVA, Paradise. To insure we can mutually lock up this long-term supply, I suggest we meet as soon as possible to work out trial dates and action steps.

We value TVA's business and look forward to helping you with the Fe fluxing application.

Yours truly,

John F. Wurster  
Vice President, Sales and Marketing

pc: John Comer



Western Coal Advisory  
Summer/Autumn 1999

## **Burning PRB Coals ADA Environmental Offers Flyash Solutions**

### **ADA-249 Fluxing Agent for Cyclone Boilers**

The WCC and PHB Hagler Bailly jointly hosted their second Powder River Basin Coal Use Seminar in St. Louis in early August. Among the topics addressed were those relating to flyash management. WCC member company, ADA Environmental Solutions, LLC (ADA-ES) has, for the past 20-plus years, been working with power plants to provide solutions to the collection of flyash from PRB coals with ESPs and baghouses. ADA-ES recently developed two new products to resolve technical challenges related to PRB coals that could further expand the number of plants capable of burning these fuels.

Cyclone boilers were designed specifically to fire Eastern bituminous coals. When utilities with cyclone boilers switch to PRB coals with low ash, low iron and high calcium, they're faced with a variety of combustion challenges, including:

- spouting from cyclones
- high furnace temperatures
- heavy convection pass fouling
- high carbon in the flyash
- increased loading to the ESP

These occur because cyclone boilers are designed to operate with a coating of molten ash and burning fuel on the walls of each cyclone barrel. It's important that the coating is thick enough and of the proper viscosity to catch and hold a significant portion of the coal particles as they enter the cyclone. This provides the proper residence time for good combustion and allows the ash in the coal to be directed to the slag taps and not in the convection pass.

The challenge with PRB coals is that they produce a slag which passes through its viscosity range from solid to very low viscosity over a small temperature range (approximately 100°F). This makes it almost impossible to operate with a suitable sticky ash layer.

To alleviate fluxing problems, some utilities are using iron pellets as fluxing agents. ADA-249 (Patent Pending), which is a blend of FeO and Fe<sub>2</sub>O<sub>3</sub>, was developed as a cost-effective alternate. This product is in a powdered form that allows for easy feeding into the belt leading to the boiler house or it can be fed pneumatically. Due to its size distribution and the cyclone aerodynamics, ADA-249 will be retained in the cyclone for sufficient time to be incorporated into the ash layer.

ADA-249's fluxing properties are very dependent on the oxidation state of the iron. In a reducing atmosphere the iron produces ash with much higher viscosity. Since iron is partially oxidized during the combustion process, this will produce an ash which has a slightly lower melting point, but with an extended high viscosity sticky region. This results in substantially more combustion in the cyclones, which translates into significant fuel savings, increased bottom ash sales, less slagging and fouling and lower flyash LOI. In addition, ADA-249 can improve radiation heat transfer in the furnace by increasing the emissivity of the deposits.



**April 18, 2000**

## **ADA-ES Tests New Boiler Product**

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Earth Sciences Inc. Subsidiary ADA Environmental Solutions (ADA-ES) this week begins testing a new "fluxing agent" added to boilers to help utilities burn Powder River Basin more efficiently in cyclone units originally designed for eastern coal.

ADA-ES will test its product at Kansas City Board of Public Utilities' 75-MW Quindaro plant, said a company exec. Though the test is officially scheduled to last roughly 60 days, ADA-ES expects the utility will purchase more of its product thereafter.

A blend of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , ADA-ES's fluxing agent helps to promote combustion while mitigating slag problems. When cyclone boilers use the lower-heat, subbituminous PRB coal rather than the eastern fuels they were built to use, they run into problems such as high carbon concentration in the flyash, increased loading to the electrostatic precipitator and difficult-to-use, runny slag. The new product should eliminate those difficulties, said the exec.

For more information, contact ADA-ES VP sales and marketing John Wurster at (303) 734-1727.